ABSTRACT BOOK

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LIST OF CONTENTS

Plenary lectures s588

Parallel sessions

- Analytical chemistry Electrochemistry, Analysis, Sample manipulation s593
- Education and History, Professional chemists Ethics, Employability, Labels s619
- Environment and Green Chemistry s635
- European Young Chemists' Network s667
- Food Chemistry Food / Agriculture / Agrochemistry / Nanotechnology, food and processing s671
- Inorganic Chemistry plus Young inorganic chemistry day s678
- Life Sciences s703
- Nanochemistry/Nanotechnology/Molecular machines, Carbon tubes, sheets, balls s729
- Organic Chemistry, Polymers – I s754
- Organic Chemistry, Polymers – II s780
- Physical, Theoretical and Computational Chemistry s807
- Solid State Chemistry Materials chemistry / New materials s832
- Special Symposium: Jam Session plus Young National Winners in Bio-Organic Chemistry s853

Poster session I s859
Poster session II s1109

List of Authors s1368
List of Keywords s1402

Plenary lecture I

PL-01

PERSPECTIVES IN CHEMISTRY: FROM SUPRAMOLECULAR CHEMISTRY TOWARDS ADAPTIVE CHEMISTRY

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Supramolecular chemistry is actively exploring systems undergoing *self-organization*, i.e. systems capable of spontaneously generating well-defined functional supramolecular architectures by self-assembly from their components, on the basis of the *molecular information* stored in the covalent framework of the components and read out at the supramolecular level through specific non-covalent interactional algorithms, thus behaving as *programmed chemical systems*.

Supramolecular chemistry is intrinsically a *dynamic chemistry* in view of the lability of the interactions connecting the molecular components of a supramolecular entity and the resulting ability of supramolecular species to exchange their components. The same holds for molecular chemistry when the molecular entity contains covalent bonds that may form and break reversibility, so as to allow a continuous change in constitution by reorganization and exchange of building blocks. These features define a *Constitutional Dynamic Chemistry* (CDC) covering both the molecular and supramolecular levels.

CDC introduces a paradigm shift with respect to constitutionally static chemistry. The latter relies on design for the generation of a target entity, whereas CDC takes advantage of dynamic diversity to allow variation and selection. Whereas *self-organization by design* strives to achieve full control over the output molecular or supramolecular entity by explicit programming, *self-organization with selection* operates on dynamic constitutional diversity in response to either internal or external factors to achieve*adaptation*.

In the process of reaching higher levels of self-organisation, CDC gives access to the generation of networks of dynamically interconverting constituents connected either structurally (molecular and supramolecular arrays) or reactionnally (set of connected reactions) or both. They define a class of *constitutional dynamic networks* (CDNs), presenting *agonistic* and *antagonistic* relationships between their constituents, that may couple to thermodynamic or kinetic processes and respond to perturbations by physical stimuli or to chemical effectors.

These concepts and their implementation in biological systems as well as in materials science will be described.

The merging of the features:

– information and programmability,

– dynamics and structural diversity,

– constitution and selection, points to the emergence of *adaptive* and *evolutive chemistry,* towards *systems of increasing complexity.*

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Plenary lecture II

PL-02

CATALYSIS AT SURFACES: FROM ATOMS TO COMPLEXITY

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Catalysis by solid surfaces is, among others, the basis of chemical industry (such as the Haber-Bosch process for ammonia synthesis from the elements), as well as of importance for environmental chemistry (e.g. car exhaust catalyst). Surface physical techniques enable with single crystals as model systems elucidation of the underlying elementary processes on atomic scale. In special cases the rate under continuous flow conditions may become oscillatory or even chaotic, and the adsorbed species may form spatio-temporal concentration patterns on mesoscopic scale. These complex phenomena are manifestations of the underlying nonlinear dynamics and may be considered as models for self-organisation in various areas.

Plenary lecture III

PL-03

DIRECTED EVOLUTION OF STEREOSELECTIVE MONOOXYGENASES AS CATALYSTS IN ORGANIC CHEMISTRY

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Enzymes have been used as catalysts by organic chemists for a long time, but this approach to catalysis has suffred from traditional limitations which include the often observed poor stereoselectivity, limited substrate scope and/or insufficient stability. Directed evolution is a protein engineering technique which provides a means to address and solve these problems. It involves repeated cycles of gene mutagenesis, expression and screening (or selection), thereby exerting evolutionary pressure on the system. Ever since the first report of directed evlution of enhanced enantioselectivity of a lipase as the catalyst in the hydrolytic kinetic resolution of a racemic ester, which we published 15 years ago (Angew. Chem.Int. Ed. Engl. 1997, 36, 2830–2832), this approach to generating catalysts for asymmetric transformation has been generalized as shown by numerous contributions from us and many other groups. Since the bottleneck of directed evolution is the screening of libraries, we have also focused on the development of more efficient ways to probe protein sequence space in the quest to generate mutant libraries of higher quality having an enhanced frequency of hits. Accordingly, Iterative Saturation Mutagenesis (ISM) has emerged as a powerful method in directed evolution, especially in the embodiment of Combinatorial Active-Site Saturation Test (CAST).

The lecture will focus on the use of ISM/CAST in the creation of stereoselective mutants of two types of monooxygenases: **1**) Baeyer-Villiger monooxygenases as catalysts in enantio- and diastereoselective Baeyer-Villiger reactions, and **2**) P450 enzymes as catalysts in regio- and stereoselective CH-activating oxidative hydroxylation of steroids and other types of compounds. None of the selective transformations presented can be achieved by synthetic transition metal catalysts or organocatalysts, which underscores the complementarity of the different approaches to asymmetric catalysis.

References:

Recent review of directed evolution of stereoselective enzymes in organic chemistry and biotechnology:
M. T. Reetz, Angew. Chem. Int. Ed. 2011, 50, 138-174.

Keywords: *asymmetric catalysis; enzymes; oxidation;*

Plenary lecture IV

PL-04

SIMULATION AND CONTROL OF PHOTOCHEMISTRY

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Fundamental photochemical processes such as internal conversion, isomerization, electron or proton transfer involve nonadiabatic dynamics which couple the nuclear and electronic motion. Development of efficient methods for the simulation of these processes and for determination of ultrafast spectroscopic observables in complex systems involving also their environment will be presented.[1] This will be illustrated by comparison of simulated and measured time-resolved photoelectron spectra of furan, allowing to unravel its underlying photodynamics.[2] The extension to the condensed phase will show how water influences the photodynamics of indole.[3]

Furthermore, we present control of photodynamics by including and tailoring laser fields within the recently developed semiclassical field-induced surface hopping (FISH) method,[4] thus allowing to enhance or suppress a chosen photochemical process. In this approach we combine quantum electronic state population dynamics with classical nuclear dynamics carried out "on the fly" without precalculation of potential energy surfaces. Our theoretical approach allows us to explore the controllability of photochemistry in complex systems and to unravel the mechanisms underlying the control of molecular processes. We illustrate the scope of the method by steering the cis-trans isomerization in prototype Schiff base molecular switches by shaped laser fields. Control of dynamics in the condensed phase by FISH method will be presented using designed laser fields that are capable to invoke fluorescence in the DNA base adenine.[5] We also show that our FISH method can be used to reveal fundamental dynamical processes responsible for optimal dynamic discrimination of the two molecular species flavin mononucleotide (FMN) and riboflavin (RBF), which exhibit almost identical spectroscopical features.[6] The selective identification of target molecules in the presence of structurally and spectroscopically similar background using optimally shaped laser fields opens prospects for new applications in multiple areas of science and engineering. As outlook, the application of optimal discrimination for label-free bioassays that take advantage of the twofold role of metallic nanoclusters for nanostructuring of ordered arrays and enhancement of absorption and fluorescence in proteins will be presented.

References:

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Plenary lecture V

PL-05

NMR SPECTROSCOPY – A CHEMIST'S TOOL FOR STUDIES OF THE PROTEIN UNIVERSE

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My research group uses nuclear magnetic resonance (NMR) spectroscopy for studies of proteins and protein complexes. In classical "structural biology", protein structure determination was primarily focused on systems of well-known biological or biomedical interest, with examples from my laboratory in the areas of oxygen transport, immune suppression, differentiation in higher organisms and neurodegenerative diseases such as transmissible spongiform encephalopathies. With the availability of the complete genomic DNA sequences of a wide range of organisms, "structural genomics" provides new opportunities by focusing on gene products with unknown functions and minimal structural similarity to previously studied proteins. A precisely formulated initial goal of structural genomics was to determine representative structures for all protein families and thus cover a large part of the protein universe with three-dimensional structures. In both structural biology and structural genomics the NMR method is complementary to X-ray crystallography by the fact that atomic resolution structures and other function-related data can be obtained under solution conditions close to the physiological milieu in body fluids. NMR thus has an exciting role in the longer-term challenge leading from the expanding protein structure universe to new insights into protein functions and chemical biology.

Keywords: *Proteins; NMR; Structural Biology; Structural Genomics;*

Plenary lecture VI

PL-06

BREEDING AND BUILDING MOLECULES TO IMAGE CELLS, ELECTRIC FIELDS, AND DISEASE PROCESSES

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Molecules to observe and manipulate biological systems and disease processes can be devised by a variety of strategies, ranging from pure chemical design and total synthesis to genome mining and high-throughput directed evolution. Examples will be chosen from my own experience, including fluorescent protein-based indicators, molecular voltmeters and photosensors, and peptides that light up tumors and nerves by fluorescence and magnetic resonance imaging. Synthetic nanoparticles that highlight diseased tissue by magnetic resonance imaging are valuable for noninvasive early detection of cancer, while analogous fluorescent probes can improve the accuracy of surgery. Successful molecules engage multidisciplinary and sculptural creativity, provide colorful images and movies, reveal new biological insights, and may eventually help diagnose and treat important diseases such as cancer and atherosclerosis.

Keywords: *Fluorescent Probes; Protein engineering; Electron transfer; Nanoparticles; Cancer;*

Plenary lectures

Plenary lecture VII

PL-07

CHEMISTRY WITH METHANE: CONCEPTS RATHER THAN RECIPES

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Four seemingly simple transformations related to the chemistry of methane will be addressed from mechanistic and conceptual points of view, i.e.: **1**) metal-mediated dehydrogenation to form metal carbene complexes, **2**) the hydrogen-atom abstraction step in the oxidative dimerization of methane, **3**) the mechanisms of the CH_4 ? CH_3OH conversion, and **4**) the initial bond scission as well as the rate-limiting step in the selective CH_3OH ? CH_2O oxidation. State-of-the-art gas-phase experiments, in conjunction with electronic-structure calculations, permit to identify the elementary reactions at a molecular level and thus to unravel detailed mechanistic aspects. Where appropriate, these results are compared with findings obtained from related, more conventional studies in solution or on surfaces. Three aspects deserve special mentioning: **1**) the prominent role of relativistic effects exerted by 5d elements, **2**) two-state reactivity as a (new) reaction paradigm, and **3**) unparalleled cluster-size and ligand effects on reactivity, all of which matter in the organometallic chemistry with methane at ambient conditions.

Keywords: *Alkanes; Cations; C-H activation; Computational chemistry; Density functional calculations;*

Plenary lecture VIII

PL-08

DISCOVERY OF METAL-CATALYZED REACTIONS FOR SUSTAINABLE CHEMISTRY

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The design of ”green” synthetic methodology and new approaches to sustainable energy are major goals of modern catalysis. We have developed a new approach to bond activation by metal complexes, involving metal-ligand cooperation of pincer-type complexes, and have discovered several environmentally benign catalytic reactions, including (**a**) ruthenium-catalyzed dehydrogenative coupling of alcohols to form esters and H_2 (**b**) hydrogenation of esters to alcohols under mild conditions (**c**) coupling of amines with alcohols to form amides with liberation of H2 (**d**) selective synthesis of primary amines directly from alcohols and ammonia (**e**) direct formation of acetals by dehydrogenative coupling of alcohols (**f**) generation of imines and hydrogen from coupling of alcohols with amines (**g**) dehydrogenative amidation of esters (**h**) dehydrogenative acylation of alcohols with esters (**i**) hydrogenation of amides to amines and alcohols (**j**) mild iron-catalyzed hydrogenation of ketones to acohols (**k**) iron catalyzed CO_2 hydrogenation to formate salts (**l**) hydrogenation of CO_2-derived organic carbonates, carbamates, ureas and formates as alternative routes for the conversion of CO_2 to methanol. These reactions are efficient, proceed under neutral conditions and produce no waste. They are catalyzed by pincer-type complexes and mechanistically involve aromatization – dearomatization of the hetero-aromatic ligand core. Metal-ligand cooperation of this type has led also to a distinct approach towards water splitting, based on consecutive thermal H2 generation and light-induced O_2 liberation, using no sacrificial oxidants or reductants, and involving an unprcedented O-O bond-forming step.

Plenary lecture IX

PL-09

DESIGN AND APPLICATIONS OF SELECTIVE REACTIONS OF OLEFINS

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Olefin metathesis catalysts have become one of the tools for the efficient synthesis of complex molecules. Until recently, the catalysts demonstrated poor catalyst controlled selectivity. Over the past couple of years, complexes based on molybdenum, tungsten and ruthenium have been discovered that will produce olefins good to excellent selectivity for the generation of Z olefins both in cross and ring closing metathesis. New ligands have been developed that result in different selectivities and open new applications of metathesis in the synthesis of an array of complex molecules.

Keywords: *olefin; metathesis; catalysts; ruthenium;*

Elektroanalytical methods - I

O-001

ARRAYS FOR GAS POTENTIOMETRY AND AMPEROMETRY

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Selectivity of gas sensors based on chemical modulation of work function depends on the affinity of the gas or vapor for the sensing material. In potentiometric sensors using organic semiconductors, it can be affected by the choice of the polymer and by the type and level of the doping. Incorporation of specific binding sites is another possibility, which proved to be successful in materials based on organic semiconductor/metal composites. The prime example of such sensing layer is composite of polyaniline and Pd for selective sensing of hydrogen in the presence of ammonia.[1] Rapid response and broad dynamic range has been obtained. Selectivity to ammonia can be tuned by the presence of ionic liquid in the polyaniline-ionic liquid gel.[2] Selectivity coefficient can be evaluated from the quantitative relationship linking partial pressure of gas and work function of the sensing material.[3]

On the other hand the selectivity of amperometric sensors is kinetic. It depends on catalytic activity of the selective layer to facilitate electron transfer between the species of interest, in preference to other species. We have been able to synthesize atomic metal/polyaniline composites in which the number of metal atoms determines the electrode kinetics.[4] The composition of our selective layers is $PANI*Au_mPd_n$ where stoichiometric factors n and m are in the range 0–8. The atomic metals and alloys follow theoretically predicted variation of the HOMO-LUMO energy gap. This control over synthesis of electroactive electrode materials offers unprecedented possibility for design of selective amperometric gas sensors.

References:

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Keywords: *gas sensors; potentiometric selectivity; atomic metals; atomic alloys;*

Elektroanalytical methods - I

O-002

CARBON NANOMATERIAL-BASED ELECTROCHEMICAL SENSORS IN MICROFLUIDIC TOTAL ANALYSIS SYSTEMS

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Carbon nanomaterials have become a much-discussed topic in chemical research after the discoveries of the remarkable properties of monolayer graphene, nanotubes and fullerenes. These nanostructures are robust, extremely conductive, and have unique electrochemical properties. These materials and others have recently been employed in chemical sensors, biosensors and reference electrodes with great success.

The wet chemistry laboratory onboard NASA's 2007 Phoenix mission performed the first wet chemical analysis of Martian soil using an array of electrochemical sensors. Currently, we are developing a microfluidic total analysis system, which is capable of delivering small volumes of calibration solutions, reagents and sample to miniaturized ion-selective electrodes for analysis. Until recently, the major obstacle in the development of this effort has been the successful miniaturization of ISEs. Miniaturization of ISEs is limited due to the high resistance of ion-selective electrodes smaller than ~0.5 mm causing large amounts of noise in the measurement. Traditionally, lipophilic salts have been used to decrease membrane resistance in ion-selective membranes, however these compounds are unstable in some instances and drastically affect sensor lifetime. It was recently shown that carbon nanofibers and graphene are effectively able to reduce the resistance of a polymer membrane.

Here we present the use of nanostructured carbon materials in ion-selective electrodes and microelectrodes for sensitive and selective sensing of geologically relevant inorganic species. The results discussed will focus on using these carbon materials, capitalizing on their unique properties. Emphasis will be placed on their chemistry and behavior within ion-selective membranes fabricated with these materials. With this work we will show that nanomaterials may provide a solution for robust microelectrode development that can be successfully deployed in extraterrestrial and other harsh environments, providing the scientific community with high accuracy analytical data and insights into the existence of possible life in these environments.

Keywords: *Electrochemistry; Nanostructures; Graphene; Nanotubes;*

Elektroanalytical methods - I

O-003

A DESALINATION BATTERY

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Water desalination is an important approach to provide fresh water around the world, although its high energy consumption, and thus, high cost call for new, efficient technologies. Here we demonstrate a novel concept of a "*desalination battery*"[1], which operates by performing cycles in reverse on our previously reported "*mixing entropy battery*"[2]. It exploits an electrical energy input to extract sodium and chloride ions from seawater, generating fresh water. It consists of a cationic sodium insertion electrode made of $Na_{2-x}Mn_5O_{10}$ nanorods and a chloride-capturing Ag/AgCl anionic electrode.

A four-step charge/discharge process allows these electrodes to separate seawater into fresh water and brine streams. In the first step, the fully charged electrodes are immersed in seawater. A constant current is then applied in order to remove the ions from the solution. In the second step, the fresh water solution in the cell is extracted and then replaced with additional seawater. The electrodes are then recharged in this solution, releasing ions and creating brine (third step). In the final, fourth step, the brine solution is replaced with new seawater, and the desalination battery is ready for the next cycle. Fresh water is produced during Steps 1-2, while Steps 3-4 result in the production of a brine stream.

The circular integral of the potential profile of a desalination battery as a function of charge state is equal to the net amount of electrical energy needed to drive the desalination. We demonstrated an energy consumption of 0.29 Wh l^{-1} for the removal of 25% salt, which is promising when compared to reverse osmosis (~0.2 Wh l^{-1}), the most efficient technique presently available.

References

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Keywords: *Electrochemistry; Nanotechnology;*

Elektroanalytical methods - I

O-004

NEW ASYMMETRIC SUPERCAPACITOR BASED ON HIGH SURFACE AREA POROUS MNO_2 AND ACTIVATED CARBON IN PROTIC IONIC LIQUIDS

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Pseudocapacitors are devices that store charges via faradic redox reactions taking place, at least to some extent, in the bulk of the electrode material. MnO_2 due to its low cost and good electrochemical performance is considered one of the most promising materials in many technological applications.

Protons and/or cations are involved in the faradic reactions leading to pseudocapacitance and many studies on metal oxide-based supercapacitors (SCs) have been limited to aqueous solutions. Considering that the energy density (E) of a SC is proportional to the specific capacitance (Cs) and the voltage (V) [$E=CsV^2/2$], one strategy to enhance the cell voltage in terms of the energy density is to replace the aqueous electrolyte with protic ionic liquids (PIL) to take advantage of their intrinsic ionic conductivity and large electrochemical window of stability. Here, two PIL obtained by a mixture of a base like 2-methyl or 2-methoxy-pyridine and an acid (TFA) were shown to sustain pseudocapacitance in MnO_2. Even if these PIL afford to obtain good Cs values, the narrow potential window of these PIL (between 0.8 and 0.6V) limits the SC to reach high energy densities (E) values.

Another strategy, to overcome this problem is to increase the cell voltage by using an asymmetric configuration that combines two kinds of electrode materials: one electrode (Carbon based) stores charge by a reversible non faradic reaction and the other one utilizes a reversible faradic reaction in a transition metal oxide (MnO_2). In this contribution, we will report on the electrochemical behavior of a hybrid AC/MnO_2 SC in PIL electrolytes. Further information about synthesis, characterization by SEM, XRD, CV and performance upon charge/discharge cycling will be reported.

Electroanalytical methods - II

O-005

MATERIALS STRATEGIES FOR ELECTROANALYTICAL SENSORS AND BIOSENSORS

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The development of efficient and reliable electroanalytical sensors and biosensors, with fast response, depends primarily on the materials used for their construction. Appropriate materials can confer enhanced selectivity and stability whilst, at the same time, increasing electrocatalytic effects for the desired species which can contribute to reducing interference problems. Nanostructured materials are essential for this purpose and can include metals, different forms of carbon, redox and conducting polymers. Their use can enhance performance and the reduction of response times by improving diffusion or reducing diffusion lengths Sensors and biosensors will be illustrated, prepared using such approaches and which are useful in the clinical, food and environmental areas.

Recent research has included using metal hexacyanoferrates and polyazine layers as electrode modifier materials and for redox mediators in biosensors.[1] The incorporation of carbon nanotubes in these assemblies has been investigated, also including nitrogen-doped carbon nanotubes. Electrocatalytic and synergistic effects are found, for example in the detection of hydrogen peroxide for oxidase-based biosensors.[2] The immobilization of functionalized carbon nanotubes by reticulation and covalent bonding in chitosan or dihexadecylphosphate film matrices has been studied,[3] giving evidence for unmediated electron transfer in biosensors. Stability is enhanced, sensitivities are higher, with comparable or lower detection limits and linear ranges.

A layer-by-layer approach using self-assembly to create multilayer modified electrodes for biosensors will also be described, particularly concerning the hyaluronic acid/myoglobin system and the minimum number of bilayers necessary to achieve efficient sensor/biosensor operation.[4]

References:

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Keywords: *Electrochemistry; Sensors; Biosensors; Voltammetry; Materials science;*

Electroanalytical methods - II

O-006

AN ORIGINAL METHOD TO PRODUCE JANUS MICRO- AND NANOPARTICLES IN THE BULK PHASE

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Janus particles are asymmetric particles. This type of particles has a lot of applications in different areas from molecular electronics, to targeted drug delivery. In order to break the symmetry and produce Janus particles, most of the technics are based on using interfaces. Just a few bulk procedures are known to produce these particles. We propose an original method to obtain Janus particles in bulk phase, based on bipolar electrochemistry. Bipolar electrochemistry is a technique which allows to perform electrochemistry at a conductive objet exposed in solution to an electric field. The electric field polarizes the object and when the potential difference is big enough, oxidation and reduction reactions can take place on the two opposite sides of the object. This technique is already used in the nanoscience field and to build analytical devices. In this contribution we use this concept to make electrodeposition. This approach allows us to produce a large variety of asymmetric compounds with characteristic features in the micro- or nanometer range. It is possible to modify either anisotropic or isotropic objects and to deposit metals, semiconductors, polymer and organic layers with a high spatial control. Due to its versatility and because these modifications are carried out in the bulk phase, this process might become a major technology for the production of Janus particles, also at an industrial scale.

Keywords: *Electrochemistry; Diazo compounds; Fluorescent probes; Nanoparticles; Polymerization;*

Electroanalytical methods - II

O-007

NANOTECHNOLOGY AND MULTIANALYTE PLATFORM FLOW SYSTEMS

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Sustainable development forms a key objective of the European Union with primary concern about natural resources (waste water management, water quality and quantity), food processing and distribution, health issues, climate change, clean energy as some key issues. This can be seen from the large number of research consortiums with current projects from the European Commission where Nanotechnology is one of the main areas with a budget reaching into millions of Euros. As a result microsystems technology with PAT, MPAT and NPAT become increasingly important in various operations in real-time and new innovations linking the different PAT systems successfully to microsystems technology may create fruitful solutions to the problems above. It will be shown how the establishment of PATLAB in Bucharest, Romania served as a catalyst for PAT, MPAT and NPAT. Different scenarios regarding the innovation, development, implementation and application of flow-based systems will be outlined. This will be compared with non-flow-based systems. Careful attention will be given to the reality of microfluidics as marketable applications with flow-based PAT, MPAT and NPAT, the incorporations of micro- or/and nanosensors as detection devices and if real-time is always possible. It will be discussed if there is any improvement in the configuration and construction of downscaled chemically devices and if the movement to remote sensing with innovation of high performance real-time intelligent interactive multi-point multi-species process analytical technological microsystems show that a marriage between these devices are possible. The reality of the current situation with possible future solutions will be highlighted and outlined.

Acknowledgements: *The authors would like to acknowledge the financial support received from the project Program Ideas PN-II-ID-PCE-2011-3-0538/2012-2014, financed by contract 100/27-10-2011.*

Keywords: *nanotechnology; multianalyte; microsystems; flow systems;*

Electroanalytical methods - III

O-008

ELECTROCHEMISTRY COUPLED TO ELECTROSPRAY MASS SPECTROMETRY

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The on-line coupling of electrochemistry (EC) to electrospray mass spectrometry (ESI-MS) provides a very powerful tool for studies of electroactive compounds and electrochemical reactions. With EC/ESI-MS it is possible to identify and quantitate electrochemically produced oxidation and reduction products[1,2]. It is also possible to utilise electrochemical reactions for preconcentration and/or ionisation of selected analytes, as well as for tagging purposes[3]. The coupling of electrochemical cells to ESI-MS, however, requires decoupling of the electrochemical cell from the ESI-MS high voltage, and is also complicated by the fact that the electrospray process itself involves electrochemical reactions. Care also needs to be taken to ensure that the electrochemically generated products do not undergo unwanted redox reactions between the electrochemical cell and the mass spectrometer[4] and to reduce the transfer time between the electrochemical cell and the mass spectrometer[5].

In the present communication, the advantages and limitations of combining electrochemistry and ESI-MS technique will be discussed based on selected applications. It will be demonstrated that the choice of electrolyte as well as the design of the electrochemical cell and the flow system, can affect the obtained mass spectra and the possibilities to detect electrochemically generated species.

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Keywords: *Electrochemistry; mass spectrometry; Analytical Methods; Oxidation; Redox chemistry;*

Electroanalytical methods - III

O-009

POSSIBILITIES AND LIMITAIONS OF AMALGAM ELECTRODES

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For the determination of electrochemically reducible organic substances, mercury is undoubtedly the best available electrode material.[1] However, mercury has some disadvantages (toxicity, low mechanical robustness, etc.) so that there is a constant search for other suitable electrode materials. Probably the most promising alternative are non-toxic and mechanically robust silver solid amalgam electrodes suitable both for voltammetry and for amperometry in flowing liquids.[2] The newly developed single crystal silver amalgam electrode[3] and other types of solid or paste amalgam electrodes can be very useful in this filed as well. Practical applications of voltammetric and amperometric determination of micromolar and submicromolar concentrations various types of organic substances (environmental polutants, chemical carcinogens, drugs and their metabolites, explosives, etc.) will be demonstrated together with construction of these novel electrodes and detectors based on various forms of silver amalgams.

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Keywords: *Electrochemistry; Amalgams; Voltammetry;*

Electroanalytical methods - III

O-010

VOLTAMMETRY OF ANTIOXIDANTS IN SURFACTANT MEDIA AND ITS ANALYTICAL APPLICATION

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Surfactants are widely put into practice of analytical chemistry at present time. Two important properties of them namely adsorption at the interface and aggregation into the organized structures are advantageously used in electrochemistry. Therefore, surfactants are able to modify and control the properties of electrode surfaces leading to changes in reaction rates and pathways. From other side, surfactants provide solubilization of organic compounds in water media and can be used in electrochemical studies.

Lipophilic antioxidants being widely distributed in foodstuff form important group of compounds playing key role in antioxidant defense system of living systems. Development of new methods for their determination is of interest. Lipophilic antioxidants are usually determined in organic media due to hydrophobic nature and the limited solubility of analyte in other solvents. Surfactant media can be used as less hazardous and versatile substitute for organic solvents in electrochemical determinations.

Voltammetric characteristics of retinol, β-carotene and eugenol have been studied in organic and water-organic media. All compounds under investigation are irreversibly oxidized on glassy carbon electrode. Effect of different types of surfactants and their concentration on voltammetric behavior of lipophilic antioxidants has been evaluated. The application of surfactant media leads to enlargement of linear working range for antioxidants determination. The decrease of low detection limits have been observed for all compounds under investigation.

Simple, express and reliable voltammetric methods for the retinol, β-carotene and eugenol determination in vegetable oils, spices, fruits and vegetables have been developed using preliminary extraction of analytes.

The application of surfactant media in voltammetry of lipophilic antioxidants allows to analyze them in water media or to decrease the organic solvent portion. The methods proposed is characterized by good reproducibility, speed and could be recommended for food quality control.

Keywords: *voltammetry; surfactants; antioxidants;*

Electroanalytical methods - III

O-011

ELECTROANALYTICAL DETECTION OF CYANOBACTERIAL HEPATOTOXINS MICROCYSTIN-LR AND NODULARIN AND THEIR INTERACTION WITH DNA

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Microcystin-LR (MC-LR) and nodularin (NOD) are among the most commonly reported cyclic heptapeptides produced by certain strains of freshwater cyanobacteria (blue-green algae), hepatotoxic for humans and animals. These hepatotoxins act mainly through the binding and consequent inhibition of serine/threonine protein phosphatases inside the liver cells. Beyond protein inhibition, other adverse toxicological effects have been reported concerning MC-LR and NOD exposure, such as intracellular glutathione alteration, reactive oxygen species production and lipid peroxidation.

The electroanalytical behaviour of MC-LR and nodularin NOD at a glassy carbon electrode was investigated using cyclic, square-wave and differential pulse voltammetry. The oxidation of MC-LR and NOD is an irreversible, diffusion-controlled and pH-independent process that occurs with the transfer of only one electron. Chemical degradation of MC-LR and NOD, upon incubation in different pH electrolytes, was electrochemically detected by the appearance of a new oxidation peak at a lower potential, mainly in mild acid media. The MC-LR and NOD chemical degradation product, formed homogenously in the buffer solution, undergoes an irreversible pH-dependent oxidation.

The electrochemical study showed that oxidation and cyanotoxins chemical degradation in aqueous media follow a complex redox mechanism, and their electroanalytical determination with a detection limit of one microgram per litre is foreseen, which will provide very important and useful data for toxicity evaluation.

The evaluation of the dsDNA interaction with MC-LR and NOD was undertaken using a dsDNA-electrochemical biosensor immersed in MC-LR or NOD solutions during different periods of time. The *in situ* evaluation of the MC-LR and NOD interaction with dsDNA using a DNA-electrochemical biosensor showed that both MC-LR and NOD caused dsDNA structural modifications in a time-dependent manner, adding more data to the studies of genotoxicity and carcinogenic potential associated to these toxins.

Keywords: *Microcystin-LR; nodularin; electroanalysis; cyanobacterial hepatotoxins; DNA interaction;*

Electroanalytical methods - III

O-012

SIMULTANEOUS NEUROTRANSMITTERS ANALYSIS USING MICROELECTRODES BASED ON PORPHYRINS

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Determination of neurotransmitters had an essential role in assessment of neurological diseases. Maps of brain can be drawn using the determination of the content of dopamine in different parts of brain tissue. Therefore it is very important to develop reliable and fast/real time methods of analysis for the simultaneous assay of neurotransmitters such as dopamine, epinephrine and norepinephrine. New amperometric microelectrodes were designed and used for the simultaneous assay of neurotransmitters. The microelectrodes used were based on porphyrins immobilized in diamond paste. The optimization of working conditions was done using cyclic voltammetry, for different electrolyte solutions (e.g., KCl, NaCl, KNO_3) at different pH values. Response characteristics for the proposed microelectrodes were determined for optimized working conditions using differential pulse voltammetry. The microelectrodes were used to determine the neurotransmitters from biological fluids, such as urine samples. The performances of the proposed microsensors were compared with the performance obtained using a graphite paste based microelectrode.

Acknowledgments: *The present work was supported by the European Commission through the DENAMIC project (Contract-No. 282957).*

Keywords: *elecroanalysis; neurotransmitters; microelectrode;*

Separation methods – I

O-127

MONOLITHIC COLUMNS FOR HPLC: USE OF NANOSCIENCE TO TAILOR THEIR POROSITY AND CHEMISTRY

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The first generation of porous polymer monoliths emerged in the late 1980s and proved to be excellent stationary phase for the separation of large molecules. Their well known advantages include ease of the preparation, robustness, high permeability to flow, mass transfer via convection, and a vast variety of chemistries. However, these monoliths had a small surface area since they lacked the mesopores. This made them quite useful for the separation of large molecules such as synthetic polymers and proteins as well as particles including nanoparticles and viruses. Thus, achieving good column efficiency for small molecules has been a challenge due to irregular morphology, a lack of mesopores, and a small surface area typical of these monoliths.

We have recently developed and demonstrated the second generation monoliths using a new two-step approach to the control of porous properties that includes hypercrosslinking reaction. This technique includes the preparation of generic monoliths followed by their solvation and rapid crosslinking. This process enables the preparation of porous polymer monoliths possessing large surface areas of several hundreds m^2/g.

Traditionally, the surface chemistry of the monoliths is controlled via copolymerization with monomers bearing the desired functionality, chemical modification of preformed monolith, and photografting of pore surface with polymer chains bearing the desired functionalities. Now, we have introduced novel approaches involving nanochemistry. For example, we modify the pore surface within our monoliths with gold nanoparticles affording columns with a specific selectivity enabling separation and/or fishing out thiol-containing compounds. We are also developing processes for the immobilization of nanostructures such as multiwalled carbon nanotubes and functionalized C_{60} nanoparticles that afford monolithic columns exhibiting high efficiency in the separations of small molecules.

Keywords: *Proteins; Polymers;*

Separation methods – I

O-128

SEPARATIONS OF “DIFFICULT” POLAR COMPOUNDS: AVANTAGES AND PITFALLS OF AQUEOUS NORMAL-PHASE AND REVERSED-PHASE LIQUID CHROMATOGRAPHY

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Increasing demand for the analysis of polar compounds in complex matrices has triggered the development of “Hydrophilic Interaction Liquid Chromatography” (HILIC) methods. The HILIC mode, which is essentially Aqueous-organic “normal-phase” (NP) chromatography, enables separation of strongly polar compounds, which are too weakly retained in the RP mode, but too strongly retained in the organic NP systems. Another reason for increased HILIC popularity is that highly organic mobile phases are usually compatible with mass spectrometry coupled to liquid chromatography. Many polar columns with (poly)oxyethylene (PEG), hydroxy (DIOL), mixed oxyethylene-hydroxy (Luna HILIC) or sulfobetaine stationary phases bonded either on unmodified or hydrosilated silica gel support, show dual retention mechanism in aqueous-organic mobile phases. The retention mechanism can be flexibly tuned to suit specific separation problems by selecting suitable mobile phase composition and by adjusting the temperature.

Commercial ZIC-HILIC sulfobetaine columns show excellent separation properties in the HILIC mode, whereas the RP retention range is rather limited in low-organic mobile phases. We prepared efficient and highly permeable (poly)methacrylate monolithic capillary sulfobetaine columns, showing, e.g., similar separation selectivity for phenolic acids and flavones as the ZIC-HILIC column in the NP mode, but significantly higher retention and improved separation selectivity in the reversed-phase mode.

A single column can be used alternately in the HILIC and RP modes by switching the acetonitrile–acetate buffer mobile phase gradient program between highly aqueous (RP)mode and highly organic (HILIC) mode. The differences in selectivity between the HILIC and the RP modes can be used to improve the separation and the peak capacity of complex samples cpntaining polar compounds in two-dimensional LC-LC. The approach was applied to the analysis of natural antioxidants in beer, wine, tea and herbal extracts.

Acknowledgement: *The support of this work by the Grant Agency of the Czech Republic under the project P206/12/0398 is acknowledged.*

Keywords: *Liquid Chromatography; Analytical methods;*

Separation methods – I

O-129

ANALYSIS OF VOLATILE FRACTION OF THYMUS PANNONICUS AND CORRELATIONS WITH INORGANIC PLANT COMPOSITION BY STATIC HEADSPACE GAS CHROMATOGRAPHY, MASS SPECTROMETRY AND ATOMIC SPECTROMETRY

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Depending on specific analytical technique producing samples, the term “volatile fraction” could be related to analytical headspace, essential oil, flavor, fragrance, aroma or extract. There is a large and usually puzzling diversity of volatile organic compounds (VOCs) emitted by plants and only partly explained functions in biotic and abiotic media. On the other hand inorganic components, especialy trace elements require a different experimental approach in analysis. For elucidation of their role and learning about possible relations with specific organic components additional chemometrics approach will be applied. Inorganic plant composition explains only a small part of variation in essential oil composition but, is there any correlation with volatile compounds sampled differently?

Fifteen plant individuals of *Thymus pannonicus* All. (Lamiaceae) were collected during flowering period in southern Banat (Serbia). Dry leaves were immediately after comminuting hermetically sealed and subjected to static headspace extraction (SHS), followed by GC and GC-MS analysis. After SHS-GC analysis, the same samples were subjected to microwave-assisted acid digestion. The resulting solutions were used for determination of several elements (Na, K, Ca, Mg, Fe, Mn, Zn, Cu, Cr, Mo, Co and Ni) by atomic absorption and emission spectroscopy (FAAS, GF-AAS and ICP-AES).

Monoterpenes dominated in all examined headspace extracts, ranging 57.85–96.11%. Extracts with monoterpene hydrocarbons as principal compounds contained limonene, myrcene, α-pinene, *E*-β-ocimene and camphene in amounts up to 42.99 %, 39.54 %, 35.58%, 23.56% and 15.81%, respectively. In oxigenate monoterpenes-rich extracts geranial, neral, 1,8-cineole and linalool were the most abundant (23.44%, 22.10%, 12.52% and 11.99%, respectively) and also contained non terpenic compounds in substantial amounts (13.15–25.20%), mainly 6-methyl-5-hepten-2-one (8.85 – 16.01%). Sesquiterpene hydrocarbons and oxygenate sesquiterpenes constituted a small fraction of analyzed headspace extracts, 1.53–5.20% in total.

The obtained results are subjected to the chemometrics analysis (PCA and CA) in order to highlight possible relationships.

Keywords: *Analytical Methods;*

Separation methods – I

O-130

DEVELOPMENT OF HYDROPHILIC INTERACTION LIQUID CHROMATOGRAPHY (HILIC) STATIONARY PHASES IN MONOLITHIC CAPILLARY FORMATS

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The interest in hydrophilic interaction liquid chromatography (HILIC) stationary phases largely lies on their potential for effective separation of small, highly polar molecules: a problem distinctly besetting conventional reversed-phase materials. Development in capillary formats could further support important micro-separation applications in pharmaceutical analysis, toxicology and proteomics, amongst others. The wide availability of monomers opens possibilities to tailor polymeric monoliths to exhibit HILIC behaviour. One of these is exploiting the zwitterionic nature of polymerisable betaines, *e.g.* N-(3--Sulfopropyl)-N-(methacryloxyethyl)-N,N-dimethylammonium betaine (SPE). The challenge lies in maximising as much zwitterionic moieties available for surface interaction as well as achieving the most favourable morphology. This study investigated the separation of selected nitrogenous bases and nucleosides in monoliths prepared by thermally-initiated co-polymerisation of SPE and ethylene glycol dimethacrylate in fused silica capillaries of different internal diameters (50–200 µm). The influence of monomer concentration, porogenic solvent polarity and polymerisation temperature on selectivity was studied. Reduction in reaction time and increase in capillary diameter have distinctly resulted in higher efficiencies. HILIC behaviour was very predominant when acetonitrile concentration in the mobile phase was higher than 70 %. The effect of buffer salt concentration and pH in the mobile phase was also demonstrated. Further optimisations are carried out, ultimately towards developing applied methods for drug analysis using LC-MS.

Keywords: *liquid chromatography; polymers; microporous materials;*

Separation methods – II

O-131

NEW FIBERS FOR SPME AND LC/MSN MONITORING OF SELECTED DRUGS AND THEIR METABOLITES

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The quantitative and qualitative determination of drugs and biologically active compound becomes more and more important in pharmacokinetic analysis and therapeutic drug monitoring. The most relevant matrices to be analyzed for this purpose are plasma or blood, due to providing a good correlation between their concentration and pharmacological effects. One of the major tools in the pharmacokinetic studies is the combination of high-performance liquid chromatography and mass spectrometry (HPLC-MS). This simple and selective method has been used for the determination of drugs belonging to different medicinal classes in human plasmaPolypyrrole (PPy) and polythiophene (PTh) SPME coatings and their derivatives with molecular template were used and their ability to extract selected drugs from different classes with different physico–chemical properties and of widely varying polarities were evaluated. SPME fibers are manufactured electrochemically by coupling the homemade electropolymerization system to a new generation potentiostat/galvanostat in three-electrode array. Physico-chemical properties, mechanical and chemical stabilities were characterized by scanning electron microscopy and infrared spectrometry. The SPME coatings were evaluated by analyzing clinically relevant antibiotic drugs – linezolid, daptomycin, amoxicillin and moxifloxacin. Important factors in the optimization of SPME were discussed. Finally, the chromatographic measurements were performed by HPLC/MS. The potential of polymeric SPME sorption coatings for selective extraction of the drugs was demonstrated considering the results obtained for the standard solutions and applied to human plasma samples.

Developed method can be used for the quantitative analysis of selected biologically active compounds, and provide a potential application to study the metabolism and pharmacokinetics of other drugs from different medical classes from the biological matrices. The results demonstrate the potential of *in vivo* SPME as a useful sample preparation tool for chromatographic based metabolomics drug monitoring in the biomedical application from patients receiving therapeutic dosages.

Acknowledgments: *This work was supported by National Science Center (Cracow, Poland), no. 2011/01/N/ST4/03178.*

Keywords: *fibers; spme; drug; metabolites;*

Separation methods – II

O-132

CHROMATOGRAPHIC DETERMINATION OF CARBOHYDRATES IN PLANTS – AN OVERVIEW OF SEVERAL ATTEMPTS

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Carbohydrates and sugar alcohols are important plant components the composition of which may markedly vary with season, light availability and status of plant growth. Apart from plant growth status, carbohydrates also reflect changes of photosynthetic activity and abiotic stress phenomena, such as hyperosmosis. In addition to plant physiology, the exact identification and reliable quantification of carbohydrates in plant material is also of growing importance for the calculation of more sophisticated carbon balances of numerous biogeochemical processes.

Today, liquid chromatography is the most suited method for the accurate analysis of carbohydrates and sugar alcohols. Carbohydrates can be subdivided in mono- (e.g. glucose), di- (e.g. sucrose), oligo- (e.g. raffinose) and polysaccharides (e.g. starch, inulin, polyfructans). The several components can be detected by either pulsed amperometry (PA), refrective index (RI), evaporate light scattering (ELS), or mass spectrometry (MS).

This presentation is based on both the research of our group [1-3] dealing with the development of analytical methods for the determination of carbohydrates, sugar alcohols and polysaccharides in several plant species, and a recent review article by myself [4].

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Keywords: *Carbohydrates;*

Separation methods – II

O-133

MOLECULAR STRUCTURE ON THE BALANCE IN THE XXI CENTURY – RAPID HIGH RESOLUTION AND TANDEM MASS SPECTROMETRY

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Understanding fundamental chemical processes requires the knowledge of the elemental composition, structure, quantity, and interaction networks of the participating molecules. The necessary molecular information on organic, inorganic and biological molecules can be deduced from the accurately measured masses of the molecules of interest and their fragments. Mass spectrometry (MS) and tandem mass spectrometry (MS/MS) are currently the best analytical methods for these undertakings. Fourier transform MS (FTMS) provides superior resolution and mass accuracy among the palette of the MS instruments. However, modern comprehensive structure analysis of molecules and macromolecules present in extremely complex biological and environmental samples and/or performed under time-constrained experimental conditions demands a substantial increase in the acquisition speed of high-resolution and high mass accuracy MS and MS/MS data. For this reason, absorption mode spectra representation has been implemented in FTMS as a part of enhanced FT (eFT) signal processing. On the other hand, filter diagonalization method (FDM) is capable of overcoming the FT resolution limitation. Recently, we described the first implementation of FDM for FTMS [1, 2] and the first application of electron-mediated MS/MS for structural analysis of intact 150 kDa monoclonal antibodies.[3] Here, we will discuss the state-of-the-art in eFT and FDM MS method development, then present and compare the advantages of eFT and FDM MS for (**i**) MS/MS-based top-down structure analysis of large intact proteins, including the monoclonal antibodies; and (**ii**) MS-based analysis of extremely complex environmental samples, e.g., crude oils and biofuels, where we will show, i.e, how eFT and FDM MS push the upper mass limit for separation of closely, e.g., 1.1 mDa (C_3 vs. $SH_3{}^{13}C$), spaced molecular peaks.

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Keywords: *mass spectrometry; proteomics; antibodies; structure elucidation; environmental chemistry;*

Life science, clinical and environmental applications

O-134

ENANTIOSELECTIVE CHROMATOGRAPHY, A KEY TECHNOLOGY IN LIFE SCIENCES

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To date there is a large set of diverse so-called “chiral columns” available from many companies which are the result of a long way of developments in academia and industry of enantioselective chromatographic materials (chiral stationary phases, CSPs) in order to master the challenge of resolving enantiomers and steroisomers in various matrices. It is an analytical task but also of preparative relevance as it is now state of the art to separate chromatographically e.g. chiral drugs up to a production scale of several tons per year.

The current standard of chiral liquid chromatography stands on several pillars, namely (**i**) the steadily increasing understanding of molecular recognition principles and thus of chiral discrimination concepts, (**ii**) advancements of material sciences in producing highly efficient and robust CSPs, (**iii**) the optimization of separation process parameters in terms of speed, sensitivity etc. in implementing LC and SFC operation modii, and (**iv**) optimising loadability and productivity to enter chemical production processes.

Central to all concepts of direct enantiomer separation techniques is the formation of intermediate diastereomeric associates of the chiral selector (SO) with the chiral target compounds, the selectands [(R)-SA and (S)-SA] which are sufficiently different in Gibbs binding energy (?G) to allow resolution. It is based on simultaneously activated intermolecular interactions of specific sites of the SO and the SA moieties characteristic for the SO and the SA molecular motifs. It all is spatially demanding and some conformational flexibility is of advantage to allow induced fit phenomena. Chemically speaking the SOs can vary widely from chiral polymers, e.g. CSPs derived from polysaccharides which are the most successful ones, to chiral monomers of charged and non-charged state. In this context our chiral ion exchanger type CSPs are unique and will be discussed more specifically in context of molecular recognition aspects and life science applications.

Keywords: *chromatography; enantiomer separations;*

Life science, clinical and environmental applications

O-135

DYNAMIC METHODS FOR FRACTIONATION OF TRACE METALS AND METALLOIDS IN THE SPECIATION ANALYSIS OF SOILS AND SEDIMENTS: A COMPARATIVE STUDY

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Continuous-flow (dynamic) fractionation has been recognized as an attractive alternative to conventional batch sequential extraction procedures for partitioning of trace metals and metalloids in environmental solids. Recently, two promising continuous-flow extraction systems have been comparatively studied, a microcolumn (MC) packed with the solid sample and a rotating coiled column (RCC) in which the particulate matter is retained under the action of centrifugal forces. Resemblances and discrepancies of two methods were evaluated by the fractionation of Cu, Pb, Zn, As, Sb, and Se according to their physicochemical mobility and bioaccessibility in soil, sludge, and sediment samples. The eluents (leachants) were applied in correspondence with three different four- and five-step sequential extraction schemes for partitioning of trace metals, arsenic/antimony, and selenium, correspondingly. The data obtained were correlated with peculiarities of samples under investigation and operational principles of RCC and MC.

In general, similar trends were found for the distribution of trace metals (metalloids) between extractable and residual fractions. However, some evident deviations were observed. The content of organic matter (organic carbon) in a sample can be regarded as an important physicochemical parameter affecting the leaching efficiency. As an example, for a forest soil sample ($C_{org} < 0.2\%$), RCC and MC fractionation lead to quite similar results for arsenic and antimony despite the different extraction conditions set by two dynamic methods. In contrary, for a dumped waste (soil) sample ($C_{org} = 11.5\%$), RCC extraction provides higher recoveries of environmentally relevant leachable fractions of these metalloids and the discrepancy of data obtained using RCC and MC methods becomes unacceptable for their harmonization. This problem may be resolved by optimizing operational parameters of extraction (e.g. sample, weight, volume and flow rate of eluents) as well as design parameters of microcolumns. In addition, a wide range of samples with variable composition and physicochemical parameters should be analyzed.

Life science, clinical and environmental applications

O-136

INVESTIGATING TRACE ELEMENT SPECIATION IN THE MARINE ENVIRONMENT USING CHEMICAL SEPARATION STRATEGIES COMBINED WITH SPECTROMETRIC DETECTION

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Instrumental analytical techniques with environmentally relevant detection limits are often the limiting factor in our ability to understand how trace elements are cycled in the marine environment, and hence determine their impact on environmental processes and ecosystem health. This presentation outlines robust methods for quantifying the different chemical forms of key elements in marine systems. Aspects of method design will be discussed, including separation strategies based on selective chemical reactions, detection techniques, analytical performance and sample presentation. The potential of the flow injection approach as a means of automating these methods for remote deployment and their capacity for high temporal and spatial resolution measurements will also be demonstrated.[1]

Examples will be used to illustrate the application of chemical separation with spectrometric detection to investigate trace element biogeochemistry. The use of sequential enzyme reactions with spectrophotometric detection to separate and quantify organic phosphorus species in estuaries will be described. Flow injection manifolds with chemiluminescence detection, incorporating solid phase preconcentration/matrix separation chelating columns, for the determination of trace metal micronutrients (iron and cobalt) in remote, open ocean environments will also be presented. Finally, TEVA extraction chromatography combined with multi-collector ICP-MS detection as a methodology for investigating the spatial and temporal distribution of plutonium isotopes in coral archives will be outlined. These examples demonstrate how chemical separation strategies combined with spectrometric detection can enhance our understanding of trace element biogeochemistry and the link between chemical, physical and biological processes in aquatic systems.

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Keywords: *biogeochemistry; marine environment; flow injection; spectrometric detection; separation strategies;*

Life science, clinical and environmental applications

O-137

CHIRAL ANALYSIS OF ACYCLIC NUCLEOSIDE PHOSPHONATES-BASED ANTI-AIDS DRUGS BY CAPILLARY ELECTROPHORESIS

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Acyclic nucleoside phosphonates (ANPs) are broadly used for treatment of virus diseases.[1] Oral prodrug of 9-(*R*)-[2--(phosphonomethoxy)propyl]adenine, (*R*)-PMPA (tenofovir), was approved for treatment of AIDS, and 1-[(*S*)-3-hydroxy-2--(phosphonomethoxy)propyl]cytosine, (*S*)-HPMPC (cidofovir), is used for treatment of cytomegalovirus retinitis in patients with AIDS. Enantiomeric purity control of these drugs is necessary prior to their medical applications. For this purpose, a new capillary electrophoretic (CE) method was developed for chiral analysis of these drugs and related ANPs-based antivirals using native and derivatized α-, β- and γ-cyclodextrins (CDs) as chiral selectors. The chiral CE analysis was elaborated using *R,S*-PMPA as model stereoisomers, for which the chiral selector, its concentration, and composition and pH of the background electrolyte (BGE) were selected.[2] The best CE separation of *(R,S)*-PMPA enantiomers was obtained in 30 mM sodium tetraborate BGE adjusted by NaOH to pH 10.0, with the addition of 20 mg/mL β-CD. Very good separation resolution, 2.18, was achieved within a short time, 9 min. The developed and/or slightly modified CE methods were applicable for chiral analysis of some related ANPs and subsequently they were employed for enantiopurity control of several batches of 9-(*S*)-[3-hydroxy-2--(phosphonomethoxy)propyl]-2,6-diaminopurine, (*S*)-HPMPDAP, and 9-(*R*)-[2-(phosphonomethoxy)propyl]-2,6-diaminopurine, (*R*)-PMPDAP. Using the UV-absorption detection at 206 nm and 254 nm, the concentration detection limits of the analyzed ANPs were in the submicromolar level. In addition, association constants of the complexes of ANPs enantiomers with CDs were determined from the dependence of effective electrophoretic mobilities of ANPs enantiomers on CDs concentration in the BGE by the non-linear regression analysis.

Acknowledgement: *The work was supported by GACR (203/08/1428, P206/12/0453), ASCR (Res. Project AV0Z40550506, RVO 61388963), and MSMT CR (Centre for New Antivirals and Antineoplastics 1M0508).*

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Keywords: *Analytical Methods; Electrophoresis; Enantioselectivity; Nucleosides; Nucleotides;*

Spectrometric methods – I

O-252

MECHANISMS OF ENERGY DISSIPATION AND ULTRAFAST PRIMARY EVENTS IN PHOTOSTABLE SYSTEMS: H-BOND, EXCESS ELECTRON, BIOLOGICAL PHOTORECEPTORS

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The fundamental property of biological systems is photostability. Without photostability no life would be possible. Molecular structures responsible for harvesting of the solar energy must be photostable and resistant to photo-induced chemical changes or must find a way for a recovery. To answer the questions about the photostability we have to understand mechanisms of relaxation and energy dissipation upon an optical excitation. There is a common agreement that such channels are provided by some special features of the potential energy surfaces including the conical intersections. The mechanism seems to be universal both for simple species such as H-bond systems, solvated electrons, and biologically important photoreceptor proteins such as bacteriorhodopsin.[1] This paper reviews recent progress of understanding light-energy collection and dissipation, with a special emphasis on the role of the vibronic coupling in H-bonded systems, solvated electrons and light-initiated biological photoreceptors. We will concentrate on the spectroscopic methods such as Raman imaging, the time resolved coherent anti-Stokes Raman spectroscopy (CARS) and the pump-probe transient femtosecond absorption spectroscopy. Detailed understanding the paths of energy dissipation will reveal mechanisms that mediate light-induced signal transduction as well as the role of photoreceptors in photostability protection and reparation mechanisms in living cells. Recently we have obtained the results on the normal and cancerous human breast tissue by Raman spectroscopy and Raman imaging.[2] The results demonstrate that Raman spectroscopy is able to accurately characterize pathology of tissue and distinguish between normal, malignant and benign types.

Acknowledgements: *The support through the NSC grants: 2940/B/T02/2011/40 and 3845/B/T02/2009/37.*

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Keywords: *energy dissipation; H-bonded systems; solvated electron; bacteriorhodopsin; breast cancer;*

Spectrometric methods – I

O-253

DIRECT OPTICAL DETCTION OF BIOMOLECULAR INTERACTION

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Reflectometry, has gained interest in recent years for monitoring biomolecular interaction processes beside evanescent field techniques. Both principles measure the product of refractive index and physical thickness. Whereas evanescent field techniques such as surface plasmon resonance or Mach-Zehnder interferometers measure changes in the refractive index through an evanescent field which is exponentially decaying into a layer next to a waveguide, reflectance measurements concentrate on the changes in physical thickness in a layer next to the transducer, which can be a glass slide or even a transparent polymer. Also thin layer metal-coated slides can also be used. Since changes in the refractive index caused by changes in temperature are to a large part compensated by the changes in the physical thickness, this method is robust against temperature fluctuations. Since the sensitivity does not decay in the range of half the wavelength as is the case with evanescent field techniques, reflectance can also easily be used for measuring nanoparticles or even whole cells. A variety of examples for the combination of interference and reflectance as tool for monitoring biomolecular interaction processes will be discussed, including their limitations and advantages; and the different possibilities ranging from spectroscopic detection to either single-wavelength monitoring or imaging of an array of spots.

In clinical diagnostics and environment using matrices such as sera or water, the detection of hormones and endocrine disruptors in samples such as milk or food will be discussed. Protein-protein interaction and receptor-ligand assays are another type of application. Thus reflectometry opens new possibilities to measure behavior of cells. Future trends, with special consideration to nanoparticles, effect-based analytics and point-of-need measurements will be given.

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Spectrometric methods – I

O-254

DETERMINATION OF HEPARIN BY SEQUENTIAL INJECTION ANALYSIS WITH SPECTROPHOTOMETRIC AND SPECTROFLUORIMETRIC DETECTION

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A perspective method of flow analysis – the sequential injection analysis (SIA) – with spectrophotometric and spectrofluorimetric detection was applied for determination of heparin.

The SIA is suitable for the serial analysis, while achieving the high sensitivity and the low consumption of all reagents (a sample including), with respect to the environment. In both cases the heparin determinations are based on the interaction between heparin and phenothiazine dye (Methylene Blue), resulting in the decrease of the absorbance in the spectral maximum (664 nm) and fluorescence intensity in its emission maximum (687 nm, ex. 297 nm), respectively, of the phenothiazine dye (Methylene Blue).

The absorption, excitation and fluorescence spectrum of the Methylene Blue were measured in the batch mode. After the optimization of the dye concentration (2×10^{-5}moldm^{-3}) and pH (7.0), the batch mode calibration was measured. Subsequently the laboratory made SIA apparatus was assembled and the influences of basic working parameters (the concentration of dye, the ratio of the batch dye and analyte volume, the volume of mixing and reaction coil) were studied. Under the optimum conditions the SIA calibration and the basic characteristic of the heparin determination were found. Other phenothiazine dyes (Azure A and Azure B) were tested for comparison under the same experimental conditions.

For the sequential injection analysis the concentration

4×10^{-5}moldm^{-3} of Methylene Blue, flow rate 2.5 ml min^{-1} for all reagents, the sampling volume of Methylene Blue and Heparin 150 + 150 µl and the volume 300 µl of mixing coil, without reaction coil, were selected as the optimum. The detection limit / repeatability for the spectrophotometric (spectrofluorimetric) detection, 54 µg dm^{-3} / 1.15 %, 25 µg dm^{-3} / 3.07 % respectively, were achieved. The similar results were obtained with other dyes; slightly better with Azure A

Keywords: *UV / Vis spectroscopy; fluorescence; sequential injection analysis; heparin;*

Spectrometric methods – I

O-255

LUMINOL CHEMILUMINESCENCE DETECTION OF AMINO ACIDS WITH ENZYMATIC REACTIONS

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The determination of amino acids is greatly important in clinical settings and food technologies such as the measurement of diagnosis of diseases in clinics and the measurement of freshness and taste of foods in food technologies. The conventional methods of detection for amino acids are pre-column labeling for High-Performance Liquid Chromatography (HPLC) of amino acids with fluorescence derivatives, or post-column labeling for HPLC with ninhydrine, but large amounts of organic solvents and an experimental step for labeling amino acids are necessary.

In this study, for the rapid and easy measurement of amino acids, luminol chemiluminescence detection method of amino acids was developed with enzymatic reactions. Aminoacyl-tRNA synthetases (ARSs) were used as the molecular recognition element for amino acids. The biosensing system for asparagine was constructed with asparaginyl-tRNA synthetase (AsnRS) for recognition of asparagine and the luminol chemiluminescence intensity was measured by way of several enzymatic reactions. By using this sensing system, up to 200 µM of asparagine could be measured selectively.

This work was partly supported by the Hiroshima City University Grant for Special Academic Research (General Studies).

Keywords: *amino acid; biosensor; protein; chemiluminescence detection; enzyme;*

Spectrometric methods – II

O-256

INTRA-OPERATIVE APPLICATION OF VIBRATIONAL SPECTROSCOPY

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Various techniques are established for biochemical characterization of tissue and for clinical diagnosis, several other methods based on new technology are under development.[1] Unfortunately, even well-established methods like histochemistry, magnetic resonance imaging (MRI), X-ray tomography, or positron emission tomography (PET), are not really suitable for regular intra-operative use. However, there is a clear need for an intra-operative diagnostics especially in brain surgery. Vibrational spectroscopy techniques (both Raman and infrared) complement the standard methods for tissue diagnostics.[2] This contribution shall review the current status of applicability of vibrational spectroscopy under intra-operative conditions.

Both Infrared and Raman spectroscopy have the potential for intra-operative use, because they can provide a biochemically based profile of tissue in real time and without requiring additional contrast agents.[3] Such marker-free techniques are particularly required, because they avoid any perturbation of the sample under investigation. Infrared spectroscopy is being used to examine freshly resected tissue ex vivo in the operating theater while the surgery is going on. The main potential in this case is the identification of the borderline between normal and tumor tissue. Other promising approaches include Raman fiber techniques and non-linear Raman methods. Raman fiber techniques can easily be combined with commercial endoscopes. Of the non-linear Raman methods, Coherent Anti-Stokes Raman Scattering (CARS) attracts the greatest research interest.

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Keywords: *Vibrational spectroscopy; IR spectroscopy; Raman spectroscopy; CARS (Coherent Anti-Stokes Raman Scattering);*

Spectrometric methods – II

O-257

LUMINESCENT ANALYSIS BASED ON THE ENERGY TRANSFER

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Sensitized luminescence spectroscopy based on the excited energy transfer became a powerful tool for sensitivity and selectivity enhancement in analysis of many biologically-active substances (BAS) and especially in bioanalysis. Three general types of electronic excited energy transfer are distinguished. First, is Förster resonance energy transfer (FRET), based on the transfer of energy between two fluorophore molecules, where one acts as an energy donor and the other as an acceptor. The emission spectrum of the donor and the absorption spectrum of the acceptor must overlap and this is a diffusion-controlled process. There is a variety of FRET fashions exists especially in a time resolve manner but most of them apply in bioanalysis.

Second strategy that has attracted considerable interest in a variety of chemical and biological applications involves use of lanthanide chelates formation resulting in exclusion the diffusion control. In such complexes, the energy absorbed by organic BAS-ligand (donor) is first transferred to its triplet state through intersystem crossing and then intramolecularly transferred to a closest resonance level of the lanthanide ion (acceptor) which finally emits sensitized fluorescence displaying “antenna” effect. Three possibilities to enhancing the lanthanide sensitized fluorescence will be discussed.

Third kind of energy transfer is sensitized room temperature phosphorescence (SRTP) results from triplet-triplet (T-T) energy transfer between the organic donor and acceptor molecules mainly in micellar solutions of surfactants. In this case two possibilities for enhancing of the analytical selectivity will be discussed: the indirect and direct SRTP analyte detection of polycyclic aromatic hydrocarbons.

The aim of the report is to reveal major factors influencing the efficiency of energy transfer in all kinds of sensitized luminescence and discuss their practical application in fluorimetric analysis of antibiotics, amino acids, anticoagulants, pesticides and bioanalysis including cell analysis.

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Spectrometric methods – II

O-258

STABILITY AND CHEMICAL INERTNESS STUDIES OF NOVEL GADOLINIUM COMPLEXES USED IN MRI

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The use of contrast agents as tools for diagnosis is a common practice during medical examinations. Their role is to improve the quality of images by enhancing the contrast between normal and diseased tissues. Gadolinium chelates are the commonly available commercial contrast agents for MRI examinations. Since Gd^{3+} is toxic in its ionic form, it has to be administered as a stable complex which can be rapidly excreted from the body.[1] To ensure that the inherent toxicity of the contrast agent is reduced, the knowledge of two physicochemical parameters are essential for the gadolinium chelate: its thermodynamic stability and chemical inertness.

In this context, our approach is to determine the thermodynamic stability of complexes by potentiometry and evaluate their inertia in the presence of competitive cations (Cu (II) and Zn (II)) by UV-visible and/or relaxometry.[2] Two candidates for MRI imaging (***i***) a macrocyclic ligand, tricarboxylic substituted benzimidazole moiety DO3A-BIM (***ii***) a linear ligand, DTDTPA,[3] will be presented.

The analysis of the results were as follows:

- from thermodynamic point of view, DO3A-BIM complexes are very stable in aqueous solution which suits well for their use in biological media.
- from kinetic point of view, the demetallation mechanisms of GdDTDTPA and its commercial analogue GdDTPA (Magnevist®) are different. Furthermore, their half-life indicated that GdDTDTPA is more inert than GdDTPA in biological environment. Therefore, GdDTDTPA associated with nanoparticles contain the properties required for use in MRI.

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Keywords: *Gadolinium; Thermodynamic stability;*

Biosensor strategies

O-259

SYNTHETIC BIOLOGY AND NEW MATERIALS FOR BIOSENSORS

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This paper now describes how synthetic biology can be employed to create and tune materials for biosensors. For example, a polyQ fibre, based on the primary RFP-polyQ$_{77}$ amyloid fibre-forming unit is described which is able to self assemble into self supporting fibrous material. The RFP demonstrates that the fibre can be made to be functional and the properties of this material are examined.

Bio-luminescence Resonance Energy Transfer materials can be created with luciferase (**a**) to shift the emission to longer wavelengths by energy transfer with a fused proten, making the assay more versatile for applications where shorter wavelengths are difficult to measure (**b**) to investigate constructs with abiotic materials where energy capture and emission can be enhanced through the use of semi-conducting nano-materials (**c**) to look at self-assembly of functional fibres containing the luminescent protein system.

BRET constructs are demonstrated between luciferase and (**i**) red fluorescent protein or (**ii**) cherry fluorescent protein. However, >50% energy transfer from the luciferase-luciferin to the fluorescent protein is difficult to achieve in a one-one construct. We examine this and propose ways to improve this yield by making the first double construct Cherry-Luc-Cherry and by other active site manipulations.

The future use of synthetic biological materials as analytical reagents is a core theme of this presentation.

Keywords: *biosensors; protein engineering;*

Biosensor strategies

O-260

ULTRA-SPECIFIC VIRUS BIOSENSOR USING REDOX ANTIBODY PROBE INTERACTION WITH NANOCHANNEL ADSORBED VIRUS PARTICLES

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Development of immune-based and DNA-based methods constitute an interesting topic for enhancing selectivity of sensor performance for environmental, biomedical and clinical analysis through the incorporation of high specificity binding agents including antibodies, DNAs and others. However, specific identification remains challenged by cross-reactivities between similar protein or DNA analytes such as between same antibody types raised against different antigens or between different antibody types raised against the same antigen. Recently, nanochannel-membrane electrochemical biosensors provide an alternative approach to achieve high sensitive and selective detection of biomolecules. At same time, the high density array of nanochannel structure permits high surface loading of biorecognition agents, over a sub-micrometer thickness membrane layer. In this talk, the recent interesting development of a much thicker (in micrometer dimension) membrane allows multiple site interactions between a traversing redox labled antibody target and surface attached protein targets within the nanochannels, will be presented. Selective identification of virus serotypes is based on the rate of diffusive movement of a ferrocene-labeled antibody probe through nanochannels immobilized with virus particles at the nanochannel walls. The time taken for the probe to elute from the nanochannels is readily measured using differential pulse voltammetry which gives a peak signal in response to the redox-labeled antibody probe and electrode fouling by the same antibody protein. This strategy exploits the large number of nanochannels to achieve large signal outputs using a low cost electrochemical setup and reusable nanoporous membranes.

Keywords: *biosensor; nanochannel; membrane; virus; differential pulse voltammetry;*

Biosensor strategies

O-261

BIOSENSORS BASED ON CARBON NANOTUBES: THE ROLE OF CALIBRATION ON THE REPRODUCIBILITY OF DEVICES

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The analytical performance of biosensing technologies has been enhanced by the incorporation of carbon nanotubes (CNT), which display excellent electronic, chemical and structural properties. Furthermore, the portability, functionality, and reliability of CNT-based biosensors have been improved, thus contributing to real-time, fast and accurate diagnosis. Recently, biosensors based on networks of CNT with field effect transistors (NTFET) have been developed to enhance the miniaturization of devices and associated advantageous characteristics. However the reproducibility of such biosensing devices has been affected when analytical data of individual devices (with the same configuration and characteristics) are compared. Such is due to the random nature of CNT, i.e., variation on their diameter and chirality and CNT density on networks. In this communication, some analytical approaches such as the calibration of biosensing devices were discussed as a way to solve the device-to-device variation; then, the reproducibility of nanomaterials-based FET devices could be improved for their practical application and commercialization. Furthermore, an additional example based on the development of NTFET devices for the detection of C-reactive protein is demonstrated, where the variation on the analytical response was checked, and a data analysis was performed to find analytical similarities among individual devices.

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Keywords: *biosensors; nanotubes; immunochemistry;*

Biosensor strategies

O-262

GLUCOSE OXIDASE-FUNCTIONALIZED MESOPOROUS ZIRCONIA THIN FILMS FOR ELECTROCHEMICAL GLUCOSE DETECTION

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We synthesized mesoporous zirconia thin films (MZTFs) by using a mixed solution in which zirconium hydroxide nanoparticles were self-assembled with a structure directing agent, F127 ($PEO_{106}PPO_{70}PEO_{106}$, EO = ethylene oxide, PO = propylene oxide). The mesostructures of these films were characterized by low-angle X-ray diffraction, scanning electron microscopy, transmission electron microscopy, and grazing incidence small angle X-ray scattering. The 3D pore structures were identified by two distinct ones with the *Fmmm* structure and the $P6_3/mmc$ structure. The *Fmmm* structure has interconnected pores and the $P6_3/mmc$ one less accessible pores. The MZTFs, formed on fluorine-doped tin oxide electrodes, were functionalized with glucose oxidase (GOx) and were studied for their potentials as electrochemical sensor for glucose. The MZTF with the *Fmmm* structure shows a large capacity for the adsorption of GOx. Thus, the GOx-functionalized electrode of this MZTF showed high sensitivity to glucose in a broad range of glucose concentration of 1 - 7 mM. The electrochemical data of this electrode suggest a surface-controlled mechanism, high degree of reproducibility, and a long life time.

Keywords: *Mesoporous film; Zirconia; Electrochemical glucose detection;*

Biosensor strategies

O-263

THE INTRINSIC NON-COVALENT INTERACTIONS WITHIN COMPLEXES OF A-CYCLODEXTRIN AND BENZOATE DERIVATIVES

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Dissociation energies and structural assignments of α-cyclodextrin (α-CD) complexes with three benzoate derivatives 3-methylbenzoic acid (3-MeBA), benzoic acid (BA) and 3-hydroxylbenzoic acid (3-OHBA) were for the first time studied by the combination of experiments and theoretical calculations. Qualitative experiments were performed for these α-cyclodextrin complexes to obtain the relative stability order that $[\text{a-CD}\cdot\text{3-MeBA}]^-$ (**1**) < $[\text{a-CD}\cdot\text{BA}]^-$ (**2**) < $[\text{a-CD}\cdot\text{3-OHBA}]^-$ (**3**).[1] Threshold collision-induced dissociation experiments were performed on a customized 24-pole Finnigan TSQ–700 tandem mass spectrometer to get absolute dissociation energies.[2] The obtained experimental quantitative non-covalent interactions for complexes **1**, **2** and **3** are 40.8, 41.1 and 41.8 kcal mol^{-1} respectively.

DFT calculations were carried out to further interpret non-covalent interactions within host-guest complexes. The bond dissociation energies for complexes **1**, **2** and **3** are 40.6, 40.7 and 44.0 kcal mol^{-1} respectively according to DFT calculations. Furthermore, hydrogen bonding interactions, such as O–H···O, C–H···O and C–H···π interactions contribute mainly for the stability of gaseous complexes. Inclusion geometries are still favored according to the experimental and computational results. The experimental stability order and absolute dissociation energies are in excellent agreement with DFT calculation results.

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Keywords: *non-covalent interactions; a-cyclodextrin; dissociation energies; DFT calculations; mass spectrometer;*

New analytical methodologies

O-264

THE INVESTIGATION OF ENERGETIC BENZALDOXIMES WITH THERMOANALYTICAL AND COMPUTATIONAL METHODS.

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3,5-dinitro-2-hydroxybenzaldehyde and 3,5-dinitro-4-hydroxybenzaldehyde were synthesized by nitration of salicylaldehyde and 4-hydroxybenzaldehyde, respectively.[1] These nitroaldehydes were converted into oximes with hydroxylamine[2] and were investigated by thermoanalytical (TG, DSC) and computational methods (G09W). It was observed from IR and MS spectra that 3,5-dinitro-2-hydroxybenzaldehyde yields 4,6-dinitrobenzoxazine by elimination of water via Beckmann rearrangment at 210–215 °C. On the other hand, 3,5-dinitro-4-hydroxybenzaldoxime was converged into benzonitrile by elimination of water at 160-190°C. The released heat for each exothermic reaction was measured analytically by DSC.

All theoretical calculations were carried out using the Gaussian G09W (revision B.01) program package.[3] DFT-based structure optimizations and frequency analyses were performed at the B3LYP/cc-pVDZ level of theory. The enthalpies of formation of both reactants and products were calculated using complete basis set (CBS-4M) method of Petersson and coworkers in order to obtain accurate energies. From the calculated heat of formations, the enthalpies of decomposition were calculated according to Hess's Law and were compared with the experimental values which were available from DSC analysis. The good agreement between the experimentally observed enthalpies of decomposition and the CBS-4M calculated values gives credence to the accuracy of the applied CBS-4M method.

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Keywords: *Oxygen heterocycles; Computational Chemistry; Elimination; Nitrides; Rearrangement;*

New analytical methodologies

O-265

SIMULTANEOUS OR INCREMENTAL IDENTIFICATION OF REACTION SYSTEMS?

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Identification of kinetic models is essential for monitoring, control and optimization of industrial processes. Robust kinetic models are often based on first-principles and described by differential equations. Identification of reaction kinetics, namely rate expressions and rate parameters, represents the main challenge in building first-principles models. The identification task can be performed in one step via a simultaneous approach or over several steps via an incremental approach.

In the **simultaneous approach**, a kinetic model that encompasses all reactions is postulated and the corresponding parameters are estimated by comparing predicted and measured concentrations. The procedure is repeated for all combinations of model candidates and the combination with the best fit is typically selected. This approach can handle complex reaction rates and leads to optimal parameters in the maximum-likelihood sense. However, it is computationally costly when several candidates are available for each reaction, and convergence problems can arise for poor initial guesses. Furthermore, simultaneous identification often leads to high parameters correlation, and a structural mismatch in one part of the model can result in errors in all estimated parameters.

In the **incremental approach**, the identification task is decomposed into sub-problems of lower complexity. In the *differential method*, reaction rates are first estimated by differentiation of measured concentrations. Then, each estimated rate profile is used to discriminate between several model candidates, and the candidate with the best fit is selected. However, because of the bias introduced in the differentiation step, the estimated rate parameters are not statistically optimal. In the *integral method*, measured concentrations are first transformed to 'experimental extents'. Subsequently, postulated rate expressions are integrated for each reaction individually and rate parameters are estimated by comparing predicted and experimental extents.

This contribution reviews the simultaneous and incremental methods of identification and compares them via simulated examples taken from homogeneous and heterogeneous chemistry.

Keywords: *Kinetics; Kinetic resolution; Industrial Chemistry; Analytical Methods;*

New analytical methodologies

O-266

SACCHARIDE PROBES FOR ENZYME ASSAYS AND MOLECULAR LOGIC

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A two-component glucose sensing concept based on anionic fluorescent dyes as reporters and boronic acid-appended bipyridinium salts as receptors was formulated by Singaram et al.[1–5] Going beyond glucose monitoring, real-time label-free fluorescent enzyme assays have been developed for sucrose phosphorylase (SPO) and phosphoglucomutase (PGM).[1, 2, 6] The assays are suitable for high-throughput screening of novel carbohydrate enzymes for industrial applications.[9] Glycoside phosphorylases and transglycosidases are biocatalysts for the glyco-sylation of small molecules which can be assayed with the saccharide probes.[10] These probes can also perform Boolean logic operations for "chemical computing". The combination of a boronic acid-appended viologen and perylene diimide was able to perform a complementary implication (IMP) / notimplication logic function. Fluorescence quenching and recovery with fructose was analyzed with a conventional plate reader and by fluorescence correlation spectroscopy on few molecule level of the reporting dye.[11] IMP and FALSE operations are able to form adder, subtractor and multiplicator logic systems, based on the saccharide probe and fructose.

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Keywords: *Sensors; Supramolecular chemistry; Enzyme catalysis; Fluorescent probes; Fluorescence spectroscopy;*

New analytical methodologies

O-267

SCOPE AND LIMITATIONS OF SURFACE FUNCTIONAL GROUP QUANTIFICATION METHODS

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Micro- and nanoparticles are emerging as key components in numerous application areas ranging from materials sciences to life sciences and medicine. Their properties and interactions with other molecules are largely controlled by the number, chemical nature, and spatial distribution of their surface functional groups. While the total number of surface functional groups determines their materials properties such as colloidal stability, the number of accessible functional groups indicates which fraction can be principally derivatized with application-relevant molecules such as peptides, proteins, antibodies or DNA.

We have quantified the total and accessible number of carboxylic acid groups on polymer particles by conductometry, ^{13}C solid-state NMR, fluorophore labeling, a supramolecular assay based on high-affinity inding of cucurbit[7]uril (CB7 assay), and two colorimetric assays based on toluidine blue and Ni^{2+} complexation by pyrocatechol violet (Ni^{2+}/PV assay), whereas the CB7 and the Ni^{2+}/PV assay were recently introduced by us as simple, straightforward and reliable methods to determine the number of total and accessible functional groups, respectively.[1] The results demonstrated that only a small but constant fraction of the surface functional groups is accessible to covalent surface derivatization independently of the total number of surface functional groups. All methods were thoroughly validated and compared with respect to reproducibility, sensitivity, and ease of use. Most importantly, absolute quantum yield measurements after fluorophore labeling indicated a major uncertainty for this routinely used surface group quantification method, which is directly relevant for biochemical assays and medical diagnostics. This comprehensive comparison of surface group quantification methods is now extended to copolymer-functionalized surfaces and different fluorescent dyes.[2]

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2. unpublished results

Keywords: *Analytical Methods; Fluorescence spectroscopy; Nanoparticles; Polymers; Surface analysis;*

New analytical methodologies

O-268

DETECTION OF ETHYLENE GAS USING CARBON NANOTUBE BASED DEVICES: UTILITY IN THE DETERMINATION OF FRUIT RIPENESS

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Ethylene as the smallest plant hormone plays a role in many developmental processes in plants. For example it initiates the ripening of fruit, promotes seed germination and flowering, and is responsible for the senescence of leaves and flowers. In the horticultural industries, the selective detection of ethylene at low concentrations is highly desirable to avoid over ripening of fruit.

Single-walled carbon nanotubes were modified with an ethylene binding copper(I) complex creating a reversible chemoresistive sensor for ethylene. The devices are able to detect sub-ppm concentrations of ethylene in a highly sensitive and selective manner and are simply prepared in few steps from commercially available materials. The utility of the sensor was demonstrated by following ripening stages in different fruits.

Keywords: *ethylene; copper; hormones; nanotubes; sensors;*

New analytical methodologies

O-269

FEASIBILITY OF ATTENUATED TOTAL REFLEXION SPECTROSCOPY IN MONITORING AND QUANTIFICATION OF ANTIBODY AND HOST CELL PROTEINS USING MAMMALIAN CELL CULTURE

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For the first time, we present a feasibility study for quantifying host cell proteins (HCPs) and monoclonal antibody (mAb) during fermentation of mammalian cell cultures, using Fourier transform infrared spectroscopy. Our method is a non-invasive alternative to traditional monitoring of protein levels by ELISA, 2D-SDS-PAGE and chromatography.

The robustness of our approach was tested with 66 NS0 and 40 CHO cell culture samples. To obtain a wide range of HCP and mAb concentrations, we treated the samples with polyelectrolytes at different concentrations for semi-selective protein precipitation. The obtained samples were measured *in situ* by attenuated total reflexion with Fourier transform infrared spectroscopy in the mid infrared range and analyzed using multivariate data-analysis.

We were able to quantify HCPs in the range of 2,000–55,000ng ml^{-1} and mAb in the range of 0.2- 1.7g l^{-1}. Obtained values of HCPs and mAb were in good agreement with results measured by HCP-ELISA or determined by fluorophore labeling, respectively, suggesting the suitability of this method for mAb and HCP monitoring and quantification.

Keywords: *attenuated total reflexion; host cell protein; monoclonal antibody; monitoring; fermentation;*

Chemometrics – I

O-418

CHEMOMETRICS FOR PRE-PROCESSING OF QUANTITATIVE PROTEOMICS DATA

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Among modern high-throughput biological methods, the measurement of protein expression has perhaps the greatest potential for providing useful information, since the proteome is most directly linked to the biological state of an organism. To date, however, this potential has not been fully realized due to the many challenges of comprehensive quantitative proteomics. These include diversity of protein properties and abundance, the number of analytes, difficulties in quantitation, the lack of standardized platforms, and the long sample analysis times. Extended analysis times are particularly problematic in the large scale biological studies needed to validate conclusions across a large number of samples. The goal of the present research is to explore methods for rapid, high-throughput screening in proteomics.

A popular platform for relative protein quantitation (comparative proteomics) is differential labelling of peptide digests from two or more biological states using isotopic tags, where the ratio of the two signals is indicative of up- or down-regulation of an associated protein. Current approaches use tandem mass spectrometry (MS/MS) to identify peptides prior to quantitation. A drawback of this method is a significant loss in mass spectrometer duty cycle to tandem scans. This presentation will describe strategies to improve throughput by relying only on MS scans to locate and quantify peptide pairs in the mixture. This presents significant challenges in dynamic signal processing to account for differences in charge state, number of tags, and isotopic patterns. The end result is a map of peptides present in the mixture, together with ion state and ratio. While MS resolution with the current instrument is generally not sufficient to uniquely identify peptides, the goal is to first locate differentially expressed proteins and then identify them by other means. Other challenges in this process, such as chromatographic alignment and peak overlap, will also be discussed.

Keywords: *Proteomics; Analytical Methods; Mass spectrometry; Peptides; Bioinformatics;*

Chemometrics – I

O-419

DISSIMILARITY BASED MODELING OF CHEMICAL DATA

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Studying complex non-linear chemical and/or bio-chemical systems, we need fast and effective methods of their modeling. As it will be demonstrated, dissimilarity representation (known also as pairwise representation) reveals data structure, which is not revealed in the vectorial representation, and thus widens the sets of possible approaches to data modeling. Performance of the dissimilarity based methods (e.g., Dissimilarity – Partial Least Squares)[1], will be demonstrated for calibration and discrimination of real and simulated data sets of different structure and complexity. Practical aspects of dissimilarity based modeling (e.g., the choice of dissimilarity measure, pre-selection of the so-called 'prototypes', and fusion of different dissimilarity measures or different data blocks) will be discussed, as well. It will also be demonstrated how the dissimilarity based methods applied to instrumental signals such as, e.g., LC-MS signals, allow applications of no-warping strategies for data modeling.

As main advantages of the proposed approach, we can mention its conceptual simplicity, flexibility, and very short computations time.

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Keywords: *non-linear modeling; analysis of variance; Euclidean distance;*

Chemometrics – I

O-420

APPLICATION OF NATURE-INSPIRED METHODS IN CHEMOMETRICS

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Natural Computing models, inspired in part by nature and natural systems, are a family of powerful data analysis methods able to transform available heterogeneous data into knowledge. They include Neural Networks mimicking the mechanisms of the nervous system,[1] general optimization techniques, such as Genetic Algorithms based on simulation of biological evolution[2], Swarm Intelligence based on simulation of social behavior of animals.[3]

In recent years, many Nature-inspired models have been successfully applied to the solution of complex problems related to signal processing, classification, clustering, feature selection, and regression.

In this communication, some successful application of natural computing to solve chemical problems will be presented and discussed. In particular, the use of feed-forward artificial neural networks to operate non linear classification in the cases where sample distribution would require complex decision boundaries will be shown. Additionally, the use of Kohonen architecture for nonlinear projection aimed at exploratory data analysis will be exemplified.

As far as Genetic Algorithms are concerned, examples of their fruitful use in variable selection will be given.

Lastly, some recent applications of a swarm intelligence algorithm (Particle Swarm Optimization) in chemometrics will be described. In particular, the use of PSO for parametric time warping, peak deconvolution and clustering will be discussed.

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Keywords: *Analytical Methods; Chemoinformatics;*

Chemometrics – II

O-421

FUSION OF METABOLOMICS DATA FOR A BETTER UNDERSTANDING OF MULTIPLE SCLEROSIS

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While Multiple sclerosis is a major disabling disease of the Central nervous System (CNS) in young adults, little is known on the real cause of this disease; Even diagnosis in an early stage is a non-solved issue.Cerebrospinal Fluid (CSF) is the bio fluid, which is in closest interaction with the Central Nervous System (CNS). It is therefore the bio fluid that best mirrors the biochemical status and processes in brain and CNS. Biochemical changes are therefore most likely to be found by means of a comprehensive analysis of the CSF Other bio fluids such as plasma may also contain crucial information;

Comprehensive analysis by a large variety of analytical technologies, yield however complex data for which chemometric data analysis and data mining have become crucial tools. Since no analytical platform on its own yields a comprehensive image of the biochemical status, data fusion has become widespread in the last decade. Many methods have been proposed, most of them restrict to a linear fusion strategy However, it is not realistic to assume that all biological or (bio)chemical data display this simple linear behavior. In that case linear methods are bound to fail. In this lecture alternative approaches will be presented. One is based on the hierarchical fusion of mid-level fusion models. Non-linear kernel fusion model allow to cope specifically with nonlinearities.[1] We use our pseudo-sample approach[2, 3] to reveal the contribution of the individual variables.

In the lecture we will present results of fusion of CSF and plasma analysis data for a better diagnosis and search for biomarkers for Multiple Sclerosis

References:

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Keywords: *data fusion; metabolomics data analysis; multiple sclerosis; chemometrics;*

Chemometrics – II

O-422

SIMULTANEOUS SIGNIFICANT FACTOR DETECTION AND VARIABLE SELECTION USING MULTI-BLOCK ANALYSIS METHODS

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Multivariate methods are nowdays widely used in the study of data matrices containing thousands or hundreds of thousands of variables. In spite of their ability to work with many correlated and noisy variables and to separate the significant variation from the noise, these methods can still be improved by a relevant selection of variables.

In this presentation, we propose to split the data variable-wise into a certain number of segments, each considered as an individual block of data, and to detect the relevant segments with a Multiple-Block method.

In the case of data sets where the values of the variables are thought to vary with the levels of experimental factors, it is possible simultaneously to detect which factors have a significant effect.

Application of the proposed methods to several data sets, increasing in complexity, has shown satisfactory results.

Keywords: *Variable Selection; Factor detection;*

Chemometrics – II

O-423

HOW TO ACCESS HIDDEN INFORMATION IN CHROMATOGRAPHIC DATA

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In chromatographic data it is often seen that one peak reflect more than one compound. Commercial software for multichannel data handling (e.g. GC-MS) often offers the possibility for performing deconvolution. However, the solutions given by such software are often unreliable and in many cases there is little or no possibility for the user to evaluate the quality of the resulting model. An alternative to the manufacturing software is fitting of Gaussian or Lorentzian models to the signal. However, the solutions from such models are not unique. Another problem is that the user must know how many compounds the model should evaluate. Another approach is to use PARAlel FACtor analysis 2 (PARAFAC2), which has previously been shown to be a powerful tool for resolution of overlapping peaks.[1, 2]

In the presentation it will be demonstrated how PARAFAC2 can help the analyst in the task with deconvolution of peaks. New developments concerning automation will also be presented. These developments enable the possibility for non-chemometricians to make models with PARAFAC2 and will result in a more unbiased result than if the models where to be evaluated manually.

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Chemometrics – III

O-424

MULTIOBJECTIVE EXPERIMENTAL OPTIMIZATION

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Most problems posed in an experimental framework have several facets to be taken into account, starting with the experimental factors and their influence in different analytical responses. These different aspects tend to exhibit a conflicting behaviour, the improvement of one of them results in deterioration of some other(s).

Instead of weighting the different responses into a single one to be optimized, the present work tackles the multicriteria optimization from its vector nature to search for the Pareto-optimal solutions, i.e. solutions that are optimal in at least one of the criteria maintaining the rest in their best allowable values. This multiresponse optimization is addressed from two perspectives.

The most usual context: optimization refers to the searching of experimental conditions to optimize several analytical responses of interest. In general, this has to be approached from an experimental perspective. Consequently, whether these responses are individually or jointly optimized, the reliability of the optimal solutions is dependent on a proper experimental design.

For some experimental procedures, above all when there are several experimental factors, the number of experiments in a standard design may make it unaffordable. Hence, the other perspective is the selection of the experimental design itself, based on its characteristics. There are several criteria to measure the quality of an experimental design (variance inflation factors, values of the variance function and related to them the alphabetic criteria). The search of a reduced design that maintains the required quality is again a problem of multicriteria optimization.

By using analytical problems as guiding examples, Pareto-optimal solutions are computed for choosing suitable experimental designs and for simultaneously optimizing several analytical responses of interest. Besides, to study the information in these optimal solutions a graphical way, an adapted version of the parallel coordinates plot, is also shown.

Acknowledgments: *Financial support through projects CTQ2011-26022 and BU108A11-2*

Keywords: *Chemometrics; Experimental design; Analytical methods; Gas chromatography;*

Chemometrics – III

O-425

COUPLING 2D-WAVELET DECOMPOSITION AND MULTIVARIATE IMAGE ANALYSIS

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Wavelet transform (WT) is mainly used in image analysis as a preliminary step for denoising or compression and/or in order to extract textural features,[1] in this case yelding global image descriptors to be used for classification or properties prediction. In the present work, we develop an approach that uses the 2D-DWT (discrete wavelet transform) multiresolution advantage in the context of defects detection in single images. The basic idea is to combine the potentiality of the MIA approach[2, 3] with the wavelet decomposition scheme to take into account pixels correlation pattern.

To this purpose, given a wavelet filter, the resulting blocks (Approximation, Horizontal, Vertical and Diagonal coefficients) from a 2D-WT decomposition of the image (DWT2 and SWT2 decomposition schemes are compared), applied separately to each color channels, are used as different "versions" of the original image capturing the different patterns present in the image. We consider a redundant representation, i.e. including approximations of every decomposition level considered. In this way, as many images as 4 times L (decomposition level) times N (color channels) are obtained. These are unfolded to obtain a data matrix of dimensions: pixels × ($4 \times L \times N$). At this point the usual MIA approach is followed, afterwards constructing multivariate control charts for Hotelling-T^2 and residual sum of squares on the basis of one or few normal operating images (NOC) so that defects can be detected in faulty ones.

The new proposal has been tested on different data sets, such as tiles images with quite difficult to detect defects, oranges images corresponding to several damages and multispectral bread images to detect surface defect. The main goal is to highlight, on one hand, the tipology of defects that can be handled by this method and how it may be used alternatively or complentary to the Bharaty and McGregor one, taking advantage of the unique features of WT, i.e. the fact that the different frequency content (related to texture) are depicted in disjoint subspaces and on the other to point out the critical aspects of the methodology.

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Keywords: *Multivariate image analysis; texture; wavelets; fault detetection;*

Chemometrics – III

O-426

CHEMOMETRICS AS A TOOL TO INCREASE EFFICIENCY OF SPECTROSCOPIC ANALYSIS OF FOOD AND ENVIRONMENTAL MATRICES

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Chemometrics is the use of mathematical and statistical methods to improve the understanding of chemical information and to correlate quality parameters or physical properties to analytical instrument data. In this study we show how chemometric methods can be efficiently coupled with two spectroscopic techniques – nuclear magnetic resonance (NMR) and ultraviolet-visible (UV-VIS) spectroscopy for analysis of complex matrices.

First, 400 MHz ^{1}H NMR spectroscopy and nontargeted approach based on principal component analysis (PCA) was applied to reveal potentially unsafe samples of unrecorded alcohol as well as for checking the floral origin of honeys, labeling of milk and milk substitute products and geographical origin of pine nuts. Validation using the independent test sets by Soft Independent Modeling of Class Analogy (SIMCA) showed correct classification in all cases.

The second direction for the application of chemometric methods in analytical spectroscopy is the quantification of substances whose signals overlap with signals of other compounds. This possibility was demonstrated by applying partial least squares (PLS) regression to quantify several parameters in alcoholic beverages such as ethyl carbamate, methanol, higher alcohols, 2-phenyl alcohol and ethyl acetate by means of NMR spectroscopy and four anions (bromide, bicarbonate, nitrate and sulphide) in sea water samples based on UV-VIS measurements.

Furthermore, we have applied different multivariate curve resolution techniques (Alternating Least Squares, Independent Component Analysis) for self-modeling decomposition of NMR and UV-VIS spectra. The performance of the algorithms was shown on several experimental case studies in food science.

The examples provided clearly demonstrate the suitability of spectroscopic measurements for analysis of food stuffs and environmental objects. The combination of these spectroscopic techniques with chemometric methods is a valuable tool to develop screening methods for checking the authenticity and quality of these samples.

Keywords: *chemometrics; NMR spectroscopy; principal component analysis; multivariate curve resolution; food analysis;*

Chemometrics – III

O-427

GC X GC-TOFMS COMBINED TO MULTIVARIATE CURVE RESOLUTION FOR THE ANALYSIS OF COMPLEX MIXTURES OF POLYCYCLIC AROMATIC HYDROCARBONS

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Comprehensive two-dimensional gas chromatography time-of-flight mass spectrometry (GC×GC-TOFMS) combined to multivariate curve resolution-alternating least squares (MCR-ALS) is proposed to improve resolution and quantification of very complex sample mixtures of polycyclic aromatic hydrocarbons. In full scan multivariate mode, different GC×GC-TOFMS data slices acquired during the analysis of samples and standards can be simultaneously analyzed and the pure component elution profiles in the two chromatographic dimensions as well as their pure mass spectra are resolved. In this case, problems ubiquitously associated to GC×GC, such as retention time peak shifting for within and between runs, are not affecting the results obtained using the proposed strategy and proper resolution of strongly co-eluted compounds, baseline and background contributions are achieved. Calibration curves can be built up using standard samples of PAHs and allow their quantification in complex oil aromatic fractions. In case of univariate detector responses like in flame ionization detection (FID) or in total ion chromatogram (TIC) mass spectrometry (MS) detection, a combination of peak alignment methods and multivariate curve resolution (MCR) is proposed for handling retention time shifts and modeling. A new “bilinear peak alignment” method based on MCR is proposed to correct for progressive within run retention time shifts in GC×GC due to the effect of the temperature program on the second dimension. In addition, Multivariate Curve Resolution-Alternating Least Squares (MCR-ALS) method under proper constraints is also proposed to analyze the already aligned bilinear augmented GC×GC data matrix for the resolution and quantification of the target compounds in complex mixtures in case of their incomplete separation and co-elution problems. The results showed the successful application of the proposed strategy for resolution and quantification of target compounds in GC×GC analysis of simulated and real samples.

Keywords: *Chemometrics; GCxGC-MS; MCR-ALS;*

Ethics and Employability of Professional Chemists – I

O-013

ETHICS AND CHEMISTRY

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Cultural development and chemical activities have always been associated with each other; mastering the conversion of matter by controlled use of energy, the Promethean gift, meant progress in humanity. All pre-historic and historic eras were associated with new chemical abilities: from the earliest phases of “unconscious chemistry”, e.g. of improving the palatability of food or of creating useful materials such as ceramics and metals, followed by a phase of “intuitive chemistry” conventionally referred to as the era of alchemy, until the mechanistic-analytical, intellectual “scientific chemistry” emerged after Paracelsus and Descartes. The historical path of chemistry culminated in the tremendous scientific advances of the 20th century, a story of the devotion of protagonists - but also of failures, controversies, and catastrophes. Nevertheless, it is exemplary for the power of internationalism, freedom-mindedness, and interdisciplinary thinking of those who were active – a success story. On the other hand, accidents and environmental problems also showed that we need, in order to progress, a more comprehensive, necessarily ethical understanding of the chemist’s activities. Chemists make chemicals – so they are responsible for them. If not, who else? Lawyers? Politicians? Economists? Obviously, in order to understand the whole truth, methods for the synthesis of the puzzle in front of us are required, i.e. the development of a holistic view. The technical prerequisites are emerging with the Internet. The main barrier is the too strongly competitive mind between those who are practicing science today. The challenge for the future is to develop the philosophy and psychology, to envisage the ideal of global fraternity/sorority, so the next generations are able to implement their full potential in cooperative modes. This way, the chemists (and other scientists) have the chance to outgrow from a magician’s apprenticeship to become true masters - largely a matter of education in science ethics.

Keywords: *Ethics; education; Chemoinformatics; History; Future;*

Ethics and Employability of Professional Chemists – I

O-014

THE MAN AND THE PROGRESS OF CIVILIZATION. WHO ARE WE AND WHERE ARE WE GOING?

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For many years, considering various philosophical trends and by acting in ecosystem we ask ourselves a weighty question: what is the environment? What is the universalism? What is the relationship between the progress of civilization and attitude of nowadays man, scholar, teacher? In a one word what is the reaction between these entities?, And how a man may find himself in this Space. Answer is not simple and its complexity does not simplify us to interpret of these phenomena, for using various types of arguments and facts that we are trying to use in interpretation of that relationship. Yes, one can recall the great names and attitudes of the world, from Confucius, by Aristoteles, Plato, Copernicus, Humboldt, Sklodowska-Curie or Czochralski, however these asked questions will be open to question and to individual interpretation.

Similar question to ask yourself: “What chemistry copies of nature? How it can be used for the civilization progress?” And in this case we will not get a straight answer, on contrary, many factors will pose a problem in precise determiniation of positive arguments relationship. Because if it is, why and for what purpose? Still, there will be an open question *Quo Vadis sciences, Quo Vadis life sciences*? Is today, by the progress of civilization and the rush towards the innovation, need a man - an interpreter? Versatile scholar? What is the relationship such as master - pupil and if the explanation of concepts in the context of sustainable development gives us a sufficient dose of information and satisfaction? This applies particularly to the attitude, behavior and seek of answers by nowadays educated man. Who we are and what we want to achieve through learning, activity, creativity and ambition?

These issues will be the subject of my discussion in the context of human-science-ethics-the progress of civilization and sustainable development.

Keywords: *man; science; civilization;*

Ethics and Employability of Professional Chemists – I

O-015

EUROPEAN WOMEN IN CHEMISTRY – A TASTE OF THE BOOK

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The publication *European Women in Chemistry* is one of the contributions of EuCheMS for the International Year of Chemistry (IYC) 2011. Its aim is to celebrate the role of women in chemistry. The book was published by Wiley VCH and we are especially pleased that Professor Nicole Moreau (President, IUPAC International Union of Pure and Applied Chemistry) agreed to write foreword to the book.

The book chapters cover women from alchemical times up to the 19 and 20th centuries, from famous and well-known women, such as Nobel Laureates Marie Curie, Irene Joliot-Curie, Dorothy Crowfoot Hodgkin, and Ada Yonath, to women whose reputations are less well-known, but whose contributions have, nevertheless, been vital. The stories reflect the range of activities and emphasise just how difficult it was for female chemists to develop rewarding careers for themselves.

Whilst there has been progress throughout the 20th century women chemists in academia and industry are still not represented well at the upper levels. There is, thus, a need to continue to promote, support and encourage women chemists and women scientists and technologists, especially those at the start of their careers. The opportunities, challenges and satisfaction of a career in European science, in general, and European chemistry, in particular, should be stated clearly to schoolchildren so as to encourage future generations. The benefits to society and to economic development from the application and exploitation of science must be clearly presented at every opportunity. This is the responsibility of each and everyone of us.

Keywords: *book; women; history;*

Ethics and Employability of Professional Chemists – II

O-016

FLEXIBLE AND MULTIDISCIPLINARY TRAINING OF YOUNG CHEMISTS

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The value of practical applications in the field of Chemistry, in either the public or private sector, is often underestimated with respect to the real possibilities that this type of formation offers.

A background knowledge of Chemistry can make decisive improvements in various sectors of production and cost considerations, especially in product improvement and production processes, the creation of quicker and safer control procedures, better packaging methods, stocking and delivery, as well as distribution chains.

In fields dealing with ecological issues, waste recycling, renewable energy, chemical risk evaluations, and scheduled plant maintenance, chemists are called upon not only to resolve technical problems, but to contribute also to the overall organization and general management of the firm.

Some concrete examples of the above assertions are presented to students, as well as teachers, in order to illustrate the ample opportunities in the workplace that Chemistry offers to young graduates with broad multidisciplinary training.

Keywords: *multidisciplinarity; risk management; stockings;*

Ethics and Employability of Professional Chemists – II

O-017

YOUNG CHEMIST EXPECTATIONS FROM A CAREER IN INDUSTRYWHAT DO YOUNG GRADUATES WANT FROM A JOB IN INDUSTRY?

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All young chemists from generation Y[1] also known as the Millennial Generation, Net Generation, … are borne between the mid-70s and the mid-2000s. In media, we often hear that youth are lazy, undisciplined, hard to manage, etc. This generation, which enters on the jobs market, is as they say? Is it really different from previous generation? How young people perceive job word? What do young graduates wait from a job in Industry? It's to these questions that we'll try to answer.

Three dimensions must be taken into consideration, which are the dimension instrumental, social and symbolic[2]. The instrumental dimension refer to material care, i.e. the wage and promotion opportunity, the social dimension concern human relation in firm and the symbolic dimension include the possibility of personal development, the ability to grow and express itself in its activity, the sense of achievement, social utility, etc. Many surveys and studies have been conduct on this topic in several countries. Conclusions are same for all; young chemist expectations are important, but not so different from previous generations' expectations. Warning! For if expectations are high, deceptions that are linked are equally important.

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Chemistry for Cultural Heritage

O-018

PRESERVING SCIENTIFIC HERITAGE: PRAGUE MONUMENTS RELATED TO HISTORY OF CHEMISTRY

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The identity of a city is shaped by various sets of characteristics by which the city is recognizable or known, like its visual image, architecture and natural setting. Less conspicuous features contribute to various parallel identities of a city, as well. Prague has been molded for centuries not only by architects, artists, musicians and artisans, but also scholars and engineers, therefore we may discover among the various identities of Prague also its scientific identity.

Material objects that constitute the scientific or in our case chemical identity of a city are, for example:

- Buildings, sites and landscapes related research and education, like universities, laboratories, observatories, hospitals, pharmacies, industrial units, etc.
- Places related to the lives and achievements of individual scholars, like birthemeteries.
- Museums, libraries and archives with collections related to the development of science and lives and work of scholars.
- Artistic objects reminding of significant personalities or important achievements in science (statues, monuments, memorial plaques).

Such physical objects are part of the world's scientific heritage and mankind's cultural memory, an area where science and humanities overlap. These items have versatile historical, esthetic, didactic and even economic values (tourism), and represent invisible links between science, technology and culture. The complex process of science and circulation and appropriation of ideas, have always been embedded in a particular setting – country, city, institution, laboratory – and performed in this setting by unique individuals, therefore these objects can serve to the historian of science as valuable tools for investigating scientific progress in its interaction with the society's intellectual, political, cultural and spiritual development. To demonstrate this, the paper focuses on Prague's chemical historical legacy in the 19th century, when chemistry and related industries became leading branches in the Czech Lands.

Keywords: *History of Science;*

Chemistry for Cultural Heritage

O-019

ALCHEMICAL CRYPTOGRAPHY

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Having had no rational way of notation, medieval European alchemists used a very complicated system of diverse graphical symbols for description of chemical substances, laboratory devices and operations. These symbols, besides their shorthand role, also serve as a specific cryptographic system, for very often the alchemists tried not only to depict their experimental results, but also to conceal them from the Christian church, avaricious noblemen and possible competitors. Origin of alchemical symbols was diverse: some symbols stood for simplified images of instruments or substances, some ones distinctly proceeded from Egyptian hieroglyphs or ancient Greek glyphs, on certain symbols influence of other graphical systems, *e.g.*, Phoenician and Hebrew alphabets, Tironian notes, *etc.,* can be traced. Of course, in most cases invention of an alchemist, usually influenced by esoteric concepts, played a not negligible role. In spite of a useful shorthand role the alchemical symbols, just due to their cryptographic effects and multiplicity, complicated intercommunication between alchemists and have complicated reading of alchemical documents up to the present days. On the other hand, the idea to describe chemical elements and compounds by certain glyphs, whose originally graphic form was step by step transformed to the alphabetical one, represented the basis of contemporary chemical logograms – probably the most perfect nomenclature system among other professional ones.

European Chemistry Thematic Network – I

O-138

THE ROLE OF ECTN AND EC2E2N IN THE DEVELOPMENT OF HIGHER EDUCATION IN CHEMISTRY IN EUROPE

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Created in 1996 as part of the Socrates-Erasmus programme, the European Chemistry Thematic Network (ECTN) is a network that brings together all the actors in higher education in chemistry in Europe (universities, national chemical societies, and the chemical industry). The network has been continuously funded under the Erasmus or LifeLong Learning programme, and the current (fifth) three-year project is called the European Chemistry and Chemical Engineering Education Network (EC2E2N), and involves both chemistry and chemical engineering higher education. There are 118 partners from 27 European countries in this project.

This presentation will outline the major activities and achievements of the network since its inception, concentrating on activities not discussed in other presentations in this session.

Past activities have included: the definition of what constitutes core chemistry in bachelor programmes throughout Europe; the creation of bachelor and master frameworks for chemistry and at the interface of chemistry and chemical engineering; identifying key generic skills; summer schools for newly appointed university teaching staff; employability of chemistry graduates; entrepreneurial skills; internet-based chemistry and chemical engineering tests at several levels and covering all areas of chemistry; linguistic issues in chemistry education; the image and attractiveness of chemistry; improving learning outcomes in chemistry and chemical engineering; and a database of chemistry programmes at bachelor and master levels as an aid to student mobility.

These areas will be briefly discussed to show how the network has played an important role in the development of higher education in chemistry over the past 16 years.

European Chemistry Thematic Network – I

O-139

VIRTUAL COMMUNITIES IN SCIENCE AND EDUCATION

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The evolution of networked distributed computing technologies is fostering the advent of virtual communities and service oriented approaches. Such evolution is bound to provide "integrated services through unified access to and seamless integration of the underlying networking, computing and data infrastructures" to research, innovation and education.

At European level distributed technologies can rely on the European Grid Infrastructure (EGI) and, for Chemistry, on COMPCHEM a virtual organization committed to design, implement and develop specific Grid services as well as tools carrying out the evaluation of the quality of the services. As to Education, a protagonist of this evolution is the European Chemistry Thematic Network (ECTN) Association that has undertaken the highly innovative engagement of pursuing long term sustainability by building a Virtual Educational Community (VEC) aimed at developing a distributed service oriented environment.

Cooperative/competitive educational approaches leveraging on the specific features of the VEC are already being adopted to allow software reuse and interoperability by developing repositories of higher education electronic teaching and learning materials and Learning Objects (LO) are being created. The most important shared patrimony of VEC is a set of electronic self-evaluation tests (EChemTest) in chemistry and related support material meant to enhance knowledge and skills in chemistry. EChemTest covers the European Core Chemistry topics at three different levels, corresponding to the end of compulsory studies and the beginning of university studies and the completion of the core chemistry syllabus in analytical, biological, inorganic, organic, and physical chemistry. Moreover, tests are provided for synthetic and computational chemistry and specialized question banks have been created for chemistry applied in cultural heritage preservation. EChemTest contents are based on a syllabus developed by analysing the major European educational system and related teaching program contents.

Keywords: *virtual community; learning object; self evaluation; compchem; service oriented;*

European Chemistry Thematic Network – I

O-140

E-TOOLS FOR THE CHEMISTRY VIRTUAL EDUCATION COMMUNITY

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Among the integrated services built for the Virtual Educational Community (VEC) established by the European Chemistry Thematic Network (ECTN) are some e-tools useful for carrying out the activities of VEC. Some of these tools are focused on the management of the knowledge developed within ECTN, on the support to the association activities and some others to communication. In this contribution we shall focus on two communication products: the Newsletter and the Magazine with the aim and the structure of the two e-tools being quite different.

The Newsletter is a way of disseminating the activities carried out by the community and illustrating their nature. ECTN has published its first "News" information in 1999, renamed ECTN Newsletter in March 2000. Following the evolution of the various ECTN projects the Newsletter has become the EC2E2N one about the end of the year 2009. At present it consists of a bimonthly electronic bulletin freely accessible on the ECTN website (*http://ectn-assoc.cpe.fr/news/index.htm*) dealing with the activities of the **ECTN Association** and the **European Chemistry and Chemical Engineering Education Network**. More in general, however, it deals also with any information related to the chemistry education in the European Higher Education Area and the extended European area. The announcement of the publication of the issues of the Newsletter is widely disseminated throughout Europe and abroad. Chemical Societies are also receiving our Bulletin, as well as the Members of the ACEN (Asia-Pacific Chemical Education Network).

The electronic magazine is a biannual publication addressed to Virtual Innovation Research Teaching & Learning Communities. The magazine is the result of a joint endeavour of the COMPCHEM Virtual Organization (VO), of the European Chemistry Thematic Network (ECTN) Association and of the University of Perugia spinoff MASTER-UP. The magazine is specialized in Molecular and Materials Science, Teaching and Learning, Computer Science research, education and innovation and focuses on Service Oriented approaches. In addition to full papers, it publishes reports of (successful or failed) attempts to build services relevant to the field of interest, lists of best practices, products used, the advantages and disadvantages of the solutions adopted will be considered for publication. In particular, all the information useful to build the puzzle of innovative complex applications in education, ICT and Molecular and Materials science are accepted.

European Chemistry Thematic Network – II

O-141

TEACHING KEY COMPETENCES TO CHEMISTRY STUDENTS – AN INITIATIVE IN THE FRAME OF THE EUROPEAN CHEMISTRY THEMATIC NETWORK

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The Budapest Descriptors, a detailed adaptation of the Dublin Descriptors in the area of chemical sciences, as well as their extension in interdisciplinary areas, are defining key competences for all academic levels. Less demanding for the first cycle, these indispensable abilities and mind-settings increase in complexity at master's and doctoral level, or for subjects at the interface of chemistry and other disciplines.

Although frequently acquired within standard study and research environments, key competences would as often be obtained by attending specialised workshops or following relevant course modules. In this context, the European Chemistry Thematic Network Association adopted a multifaceted scheme for supporting young scientists in their attempts to enter a globalised labour market.

The structure implemented consists in Centres for Key and Specific Competences in Science, addressing generic skills and attitudes, necessary for effectively responding to requirements set by stakeholders. In the same frame, Units on Languages for Specific Purposes handle linguistic issues. The Centres apply a hybrid operation pattern, combining wide-ranging e-learning possibilities to systematically organised intensive schools.

The on-line educational environment is designed on the basis of a three-fold pattern, encompassing a preliminary study phase; videoconferencing frontal hours; and post-course training and self-assessment opportunities. In this context, a specially developed web portal has been established.

The intensive schools on key competences for scientists are structured as tailor-made interactive workshops and problem-solving classes, preparing young scientists from all over Europe for the conditions encountered in the labour market.

The feedback to this two-fold activity of the Centres for Key and Specific Competences in Science, consisting in the evaluation of questionnaires, did not present noteworthy discrepancies, except for the somehow different expectations formulated in each academic level.

Keywords: *key competences; e-learning; intensive workshops;*

European Chemistry Thematic Network – II

O-142

INTENSIVE SCHOOLS AND UNITS ON LANGUAGES FOR SPECIFIC PURPOSES – HYBRID EDUCATIONAL INITIATIVES IN THE FRAME OF THE EUROPEAN CHEMISTRY THEMATIC NETWORK

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In the frame of most educational initiatives taken by the European Chemistry Thematic Network Association at a transnational level, crucial open questions have been the harmonisation of student knowledge and competences in intensive programmes; and the communication gap in the multi-lingual European environment. An efficient low-cost answer lies in implementing a hybrid scheme, combining e-learning activities and intensive face-to-face training.

The intensive schools address students and professionals, wishing to acquire a solid knowledge on the ways chemical sciences are applied in safeguarding tangible works of art. A multinational team of experts deliver frontal lectures, problem-solving classes and hands-on experimental exercises to attendees originating from Europe and beyond. Being highly interdisciplinary and international, the schools are confronted with serious complications while attempting to form levelled classrooms; a further permanent concern being how far the overload of information will not too quickly be discarded. Both problems are met with the implementation of a virtual campus combining synchronous and asynchronous techniques; and presenting
e-learning possibilities for self-paced pre- and post-school use.

A closely interrelated activity is the implementation of Units on Languages for Specific Purposes, divisions of pertinent Centres for Key and Specific Competences in Science. In their context, a web portal on key competences for scientists has been developed, including a well-built learning and self-assessment section for English as a foreign language. Moreover, synchronous training is served by an especially designed manual on teaching languages for chemists & chemical engineers. In a parallel way, intensive schools include structured language courses on topics relevant to their curriculum; pre- and post-school study and self-assessment benefiting from appropriate web-portal contents.

The feedback to these parallel activities, consisting in the evaluation of questionnaires, permits judging the efficiency of hybrid educational schemes in intensive training and in language teaching.

Keywords: *intensive schools; virtual campus; languages for specific purposes;*

European Chemistry Thematic Network – III

O-143

A ROADMAP FOR EUROLABELS IN CHEMISTRY

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Chemistry was one of the subjects which was involved since the beginning in the project "Tuning Educational Structures in Europe". Thus the Chemistry Subject Area Group in Tuning, run by ECTN, thought and discussed for many years about how chemistry degree structures across Europe could be made compatible.

From there it was a short step to consider the aspect of quality assurance. We soon realised that, although accreditation was set to become a normal feature of degree programmes in many European countries, the international perspective was missing completely.

Thus we decided to set up our own QA labels, the Eurolabels®, with the support of the EU Commission. First came the Eurobachelor®, then the Euromaster®, and work has just been completed on a Label for doctoral programmes.

This talk will outline the development, past and present, of the Eurolabel®concept.

European Chemistry Thematic Network – III

O-144

ENTREPRENEURIAL ATTITUDE: WHAT WE ALREADY TEACH AND WHAT NOT (YET)

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We educate high-level scientists. Do all our graduates need entrepreneurial skills? Can we really improve their employability by stimulating entrepreneurial attitude? A recent workshop took inventory.[1] Here we report on the results of this workshop.

Although promotion of entrepreneurship may appear to be of peripheral importance to universities committed to advancing science and humanities, entrepreneurs can anchor intellectual endeavors in reality by deploying the practical output of knowledge. Given the role of entrepreneurship in economic growth and social progress, the training of entrepreneurs can be deeply connected to public service, central to the mission of universities.[2]

Key recommendations of the workshop are:

Graduates should be better trained to think in processes. Improvement in this field does not require new components in the curriculum; it only requires a new approach in the educational process.

Teaching entrepreneurial skills is not only about setting up a company. Entrepreneurial skills are extremely useful in any job, including jobs in administration.

A severe challenge is the business plan. A business plan is similar to a project plan, which should be established for any larger undertaking within the study programme - like a thesis. A project plan including well define milestones and including a plan B in case the milestones cannot be met would be helpful to reduce extended study times in several cases.

Stimulating entrepreneurial skills is a necessary step during the educational process. Guidance for young entrepreneurs is similarly important to anchor intellectual endeavours in reality.

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History of Chemistry

O-270

HISTORICAL AND PHILOSOPHICAL APPROACHES TO THE TEACHING/LEARNING OF SOME FUNDAMENTAL CHEMISTRY CONCEPTS.

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By the middle of the 20th century, there was a profound change in science education, both in curricula and in methodological approaches. In what chemistry was concerned the curricula started giving more emphasis to a conceptual approach than to factual chemistry, in an attempt to get better trained scientists, what made the study of chemistry much more difficult for students and also more distant from the real world. This led to a new change in curricula, in view of making chemistry more appealing to students, with the idea that chemistry education should be aimed at forming citizens, and not specialists, capable of understanding and participating in public discussions about important problems related to chemical issues. And so a new trend appeared in the curricula, derived from the so called STS approach, meaning Science, Technology and Society, and later on STSE approach, which adds Environment. This approach stresses the importance of contextualizing chemistry concepts in terms of technology and society, integrating aspects of daily life and environmental concerns. Some curriculum developers also stressed the importance of history and philosophy of science that, besides allowing students to get a more general perspective of science could be useful didactic tools for the teaching and learning of several topics.

The importance of history and philosophy of science in scientific education has been gradually recognized in the last years. In the case of chemistry, the historical evolution of some fundamental concepts, like acid, oxidation, atom, valence, mole, complemented with a philosophical reflection on them and on the process of the construction of this science, may facilitate students' understanding of our modern way of viewing these fundamental concepts. History and philosophy of science also can allow clarifying the meaning of the duality theory-experimentation that accompanied the development of chemistry, and also the fruitful dialog between science and technology.

Keywords: *History of chemistry; Philosophy of chemistry; Chemistry education;*

History of Chemistry

O-271

YOU ARE MADE UP OF ELEMENTS. A THEATRICAL PERFORMANCE OF THE PERIODIC TABLE OF THE ELEMENTS FOR THE RESEARCHERS NIGHT

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In the context of the "International Year of Chemistry" celebrated last year, an entertaining play about the story of the periodic table of the elements has been written and successful performed in several Spanish cities as a vehicle for highlighting the contribution of some researchers to the development of science, chemistry in particular. The text has been written by Antonio Marchal, Professor at the University of Jaén and the stage adaptation of the script has been carried out by Noelia Rosa, a local actress who has ensured that the actors and actresses were fully identified with the characters, some of them from different countries and in different historical contexts. All this despite its unscientific education. Thus, the story has brought alive, among other characters, Antonio de Ulloa and Juan Jose Delhuyar, the only Spanish researchers who have been credited with having discovered, respectively, platinum and tungsten, Marie Curie who discovered two radioactive elements, radium and polonium, and scientists Dimitri Mendeleev and Lothar Meyer, who, working independently, put in order all the known elements and thereby facilitated the study of their properties, leading to the establishement of Periodic Table of the Elements that we all know and study.

To emphasize the educational value of the play, we have developed a few questions that we think might help study the topic of the Periodic Table and that can be answered, before the performance, during and at the end of it in class. Furthermore, the Unit Scientific Culture at the University of Jaen has edited the text of the play along with the recording of the first performance in order to enable the play to be represented and adapted to the characteristics of students in all schools who request it.

Keywords: *history of science;*

History of Chemistry

O-272

THE INTERNATIONAL CONGRESS OF APPLIED CHEMISTRY, 1912: DIFFERENT VIEWS ON THE ROLE OF SCIENCE IN FEEDING WORLD POPULATION

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Two notable events in the history of chemistry happened in Europe and United States during the year 1912: (**a**) the foundation of the International Solvay Institutes for Physics and Chemistry by Ernest Solvay (Brussels) and (**b**) the International Congress of Applied Chemistry that took place in U.S.A. The object of the Eighth Congress of Applied Chemistry (Washington and New York, September, 1912) was the advancement of all applications of chemical science to practical life. This work concerns lectures delivered by two European chemists: August Bernthsen (Krefeld, 1855 – Heidelberg, 1931) and Giacomo Ciamician (Trieste, 1857 – Bologna, 1922). They expressed different points of view about the role of chemistry in feeding growing world population. The American press followed the meeting with interest, stressing differences between the speakers. On September 12, two *New York Times* headlines drawn the attention of the reader: *Gives Out Secrets of Making Ammonia* and *Sun To Do Work of Steam*. The speeches by Bernthsten and Ciamician were the subjects. Speaking about "Synthetic Ammonia", Bernthsen (Badische Co.) informed the Congress that problems for the synthetical manufacture of ammonia from the elements were solved. BASF promoted the technical work and, in order to meet the farmers requirements of nitrogen fertilizers, the first factory for synthetic ammonia was rising at Oppau. Unlike Bernthsen, Ciamician trusted less to the fulfillement of an happy future in synthetical discovery than to resupplying the earth with the energy which it is gradually losing. Ciamician pointed out that coal deposits were not endless and that people should ask themselves whether coal was the only energy source that could benefit civilization. The answer was to be found in the fact that most of the energy which the earth receives from the sun is wasted. Ciamician's lecture "The Photochemistry of the Future" proposed a change in perspective.

Keywords: *History of Science; Photochemistry; Industrial Chemistry;*

History of Chemistry

O-273

EUROPEAN CONGRESS? EUROPEAN SOCIETY? … AND THE FIRST INSTITUTE OF TECHNOLOGY SINCE 1762

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The town of Banská Štiavnica (Banska Stiavnica, Schemnitz, Selmecbánya) was in Middle Ages the main producer of silver and gold in the Kingdom of Hungary, a part of Austrian-Hungarien Monarchy, nowadays Slovakia. The place was called "terra banensium" (the land of miners) as early as in 1156 and gained the status of a royal town in 1238. The town Banská Štiavnica was a foremost center of innovation in mining industry, in 1627 gun powder was used here for the first time in a mine and water reservoirs and channels, known as tajchy, were designed to drain water from the flooded mines and also to provide energy for the early industrialization. In 1735, the first mining school in the Kingdom of Hungary was founded there and in 1762 the Hofkammer in Vienna, with support from Queen Maria Theresa, transformed the school into the famous Mining Academy, establishing the first institute of technology or the first technical university in the world. Department of chemistry and mineralogy was formed as the very first one and his head was Nicolaus Jacquin from Leyden, who joined theory with practice and lectures were based on his own laboratory experiments. The school organized in 1786 in Sklene Teplice also the First International Scientific Congress, where even Lavoisier participated, who considered Jacquin as the founder of experimental education in chemistry. At this meeting, the first International Society "La Société de l Exploration des Mines" was also established. The most prestigious credit was given to the Mining Academy by Fourcroy in French National Convent in 1794, appreciating laboratory experiments in chemistry education. The Mining Academy in Banská Štiavnica became an example for establishing Parisien Polytechnique and other polytechnics in Europe and today we are celebrating 250 years of this tradition.

Associated Universities:

Miskolci Egyetem Bányamérnöki Kara Miskolci, Hungary

Nyugat-Magyarországi Egyetem Erdmérnöki Kara Sopron, Hungary Montanuniversität Leoben, Austria

Hornícko-geologická fakulta Technické univerzity Ostrava, Czech Republic

Fakulta baníctva, ekológie, riadenia a geotechnológií Technickej univerzity v Košiciach, Košice, Slovakia

Lesnícka fakulta Technickej univerzity vo Zvolene, Zvolen, Slovakia

Education in Chemistry – I

O-274

CHEMICAL, LIFE AND ENVIRONMENTAL SCIENCES MEET BUSINESS ETHICS, CORPORATE SOCIAL RESPONSIBILITY: AN INTEGRATED APPROACH AND PERSPECTIVE SHAPES AN ENTIRE UNIVERSITY

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IHI Zittau is dedicated to academic research, studies, and cross-regional cooperation providing an intercultural focus for (graduate) students from nearby Cz/D/PL border triangle, and elsewhere abroad. This implies intercultural education and intense foreign language training. E.g., students of project management are made aware of their sphere of responsibility (influence) and thus to keep environmental and social standards during production. On various levels, (MSc/MA/MBA, PhD, Habilitation), we strive to educate responsibly acting professionals, in turn confronting students of life sciences with ethical and economic drawbacks.

What kind of ethics do we talk about? If ethics, ethical and responsible behavior, including issues of scientific integrity, were taught just in an abstract principle-based approach one would spread vague ideas and probably disappointment among students: rather than considering ethics an integral part of their professional life, this would be perceived as an demand put exogenously on them by principles remote from their own personal and professional situation. The students hence are expected to regard ethical criteria and demands from other spheres while subjected to professional tasks in their particular business.

Practically this integrative approach is pursued by cooperation with real enterprises and other organizations. There, outside our rooms and labs, most of our MSc/MA and PhD theses are prepared, and there a graduate or postgrad gets familiar with "real-life" problems, including ethically relevant drawbacks such as environmental damages due to possible scale-up of their approaches and innovations.

Philosophically, this goes in line with modern concepts of ethics, particular dialogue ethics, which rest on three pillars of modern philosophy, i.e. (**a**) the linguistic turn, (**b**) practical turn, and (**c**) cultural turn. In sum, the cultural-based approach to ethics means that students have to develop a practical (chemical, economic, etc.) professional culture rather than learning theoretical principles.

Keywords: *ethics; transdisciplinary education; scientific and enterprise responsibility;*

Education in Chemistry – I

O-275

ASSESSMENT OF TOPICS DEEMED RELEVANT IN A NURSING CHEMISTRY COURSE

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This two-stage study focused on the undergraduate nursing course that covers topics in general, organic, and biological (GOB) chemistry. In the first stage, the central objective was to identify the main concepts of GOB chemistry relevant to the clinical practice of nursing. The collection of data was based on open-ended interviews of both nursing and chemistry teaching faculty as well as practicing nurses. From the resulting interviews, three themes emerged: topics that are Important – have a direct application in the nursing clinical practice; topics that are Foundational – are not directly important for the nursing clinical practice but facilitate the understanding of the important topics; and topics that are Not Important – do not have a direct application or are not significant in the nursing clinical practice. Utilizing the data collected, a list of clinically relevant chemistry concepts was developed. The resulting list was then evaluated by nursing and chemistry faculty at the national level.

The second stage involved the design and development of an assessment in the form of a concept inventory. The General, Organic, and Biological Chemistry Concept Inventory (GOB-CCI) is a 47 item multiple-choice instrument designed to assess students' conceptual understanding of the main chemistry concepts identified as essential in clinical nursing practice. Items for this instrument are based on the most relevant concepts as identified in the first stage of the research. In producing the current version of the instrument, data from a large-scale (n~600) pilot study was used to evaluate and edit each item. A psychometric analysis performed on the data was used to evaluate validity, reliability and item statistics. It is hoped that data from this instrument will facilitate the assessment of the GOB chemistry curriculum and courses as well as providing chemistry instructors a better understanding of the difficulties their nursing students have in chemistry.

Special symposium: Ethics in Science – I

O-276

MODERATION AND COMMON SENSE

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Seventy-five years ago chemists were depicted in movies as absentminded benign scientists who worked day and night in the laboratory immersed totally in their experiments and oblivious to the world around them. The stereotype was neglecting his family, if he had one, and was exuberated by making a new discovery. Nowadays, chemists are more social, but especially many of those in the Ivory Tower, they still do research for the sake of research and not necessarily for helping our everyday life. Frequently, the goal of the research is to get recognition and awards.

Today the image of the "mad scientist" disappeared. The media now increasingly concentrates on any negative effect of chemistry on the environment. The side effects whether true or not receives headlines, while the benefits of chemical discoveries are relegated at best to the back pages. The effect of DDT on bird's eggs was considered hundred times more important than the eradication of mosquitoes, which were responsible of millions of people dying of malaria.

The public image of chemistry has declined during the past twenty-five years. It is "politically correct" to vilify chemicals. We should not ignore the possible side effects of chemical discoveries, but we must continuously communicate to the population the hundreds benefits chemistry provides to our life. Obviously, nothing is perfect in life and there is no zero risk. However, even when chemicals sometime may contribute to the problems, chemists develop new chemicals to decrease or eliminate them. Poor public image decrease funding for research and frequently direct our students to select chemistry as their profession. The lecture will highlight responsibilities of chemists both in research and communication using common sense and moderation.

Keywords: *Public Image; Scientific responsibility;*

Special symposium: Ethics in Science – I

O-277

LIVING ETHICS FOR THE GLOBAL CHEMISTRY YOUTH

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The philosophy of the Cosmic Reality, known as the teaching of "Living Ethics" (German: *Lebendige Ethik*, French: *Éthique de Vie*) by the Russian thinkers Elena I. and Nicholas K. Roerich gives a theoretical basis for understanding the cosmic evolution, its features and the place of humankind in this process. The Roerichs' work consists of 15 books written between 1924 and 1937 (with unknown co-authors) on the main principles of new cosmic thinking. E.I. and N.K. Roerich believed that the proclamation of a coming new world was their task, an awakening of humanity which they said to be in deep crisis. The Living Ethics is in continuity with the principles of classical Indian philosophy, of Buddhism, Taoism, Confucian teachings, Christianity, and of the philosophy of Plato. The ideas of cosmic thinking and the modern scientific image of the world are briefly summarized: (**a**) evolution as a central idea in the ontology of Living Ethics; (**b**) the invisible world, an aggregation of other states of matter; (**c**) the universality of the principle of vibration (superstring theory); (**d**) the multidimensional universe with the latest observations indicating a non-Euclidian geometry of the universe and, according to some models, of a dodecahedral dimension; (**e**) Big Universe or Multiverse; (**f**) perspectives for the space-time; (**g**) the phenomenon of life, the origin of mind; (**h**) the Mind as the primary creative power of the Universe; (**i**) experiment and consciousness. Evolution is approaching *the point of singularity* where its rate reaches an infinite value, and its character must change in the near future. Our scientific-technical scope is becoming so vast that simple rational answers will not be sufficient to cope with its complexity; the Roerich's humanity or Living Ethics may present a solution.

Keywords: *Living Ethics;*

Special symposium: Ethics in Science – I

O-278

BETRAYAL IN THE LAB – INTERNAL ETHICS OF SCIENCE

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Science ethics is one of the relevant and often debated fields in the area of "*Applied ethics*". Apart from several controversies it is agreed upon distinguishing two levels of ethics: **Internal ethics** as *role ethics* focus on the behavior of a scientist within the scientific community, whereas **external ethics** as *causal action ethics* describe the implications and external concerns of a scientist's actions. While the latter are addressed by technology assessment (involving sociology, regulatory issues, governance, and others), this presentation focusses on the former approach, dealing with issues of fraud, betrayal and other kinds of misbehavior that, unfortunately, are more up-to-date than ever.

Recently several prominent examples of betrayal in scientific practice are publicly discussed. Betrayal in this context means either deceptive behavior such as forgery and invention of research results, the publication of other people's results under the own name (plagiarism), or insufficient information about references and knowledge or finance sources. According to a poll by *Nature* in 2005, 30% of the 3200 participating scientists confessed to have betrayed already in one or another way. Motives reach from academic publishing pressure to financial incentives of sponsors. Ethical values (or virtues) that make a stand against this phenomenon are **intellectual honesty** and **truthfulness**, bringing the scientist to commit himself to **objective truth seeking** and **truth assurance**.

Another aspect often raised is the call for **objectivity** and **dedicated disinterestedness**. The selfless devotion to the ambitious goal of knowledge increase should not be blurred by selfish careerism or the interests of any sponsors. Methods for obtaining these ideals are **systematized doubt** and **disciplined self-control**. Apart from that, it is justified to expect **fairness** from a scientist towards his colleagues and competitors.

Keywords: *Sustainable Chemistry; Ethics of science;*

Special symposium: Ethics in Science – I

O-279

ETHICAL PROBLEMS IN SOUTH AFRICAN EDUCATION

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The political transformation since 1994 has solved major ethical and moral issues in South Africa. However, a number of well-intentioned but ill-conceived initiatives have wreaked havoc in primary and secondary education. Consequently, tertiary education is threatened. The universities are overwhelmed by poorly prepared, academically illiterate students. Government subsidy is determined by the number of students passed and the number of ISI publications, irrespective of quality. So we neglect the bright and waste energy on the weak. The National Research Foundation is baffled by an inverse relationship between the number of publications and the number of patents. Research for the subsidy has replaced research for curiosity or utility at many universities.

Without students very little funding is available for research to build our CVs and careers. Should I write the student's thesis myself? Either I do so or accept a poorly written script. Some researchers claim that it is easier to do the research as well. Scientific careers are built on a plethora of trivial papers.

A principled approach might carry a price tag. Mediocre and dishonest bureaucrats, often in well-entrenched positions, do not tolerate criticism. It is easy to make enemies who can destroy your career. If you resist too much, you will be replaced by a less well qualified person who will pass more students. Is it ethical to claim to be an excellence driven university when this is the case?

In my opinion, speaking out against wrongs, unethical practices and dishonesty is the ultimate ethical requirement. Ethical behaviour requires actions that are not in our short-term interest. Should I show empathy towards poor students and take non-academic issues (poverty and lack of background) into account and pass their poor academic skills on to their future employers and society at large? How do I act in everyone's best interest?

Keywords: *South African Education; Chemistry Ethics; Subsidy Driven Research;*

Special symposium: Ethics in Science – II

O-280

CULTURAL RESTRAINS OF SCIENCE

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Humans invented two strategies to dominate the world: science and culture. Those two components of civilization are often in conflict.

Culture is older. Social groups always functioned basing on beliefs which may be objectively false but determine the social activities and norms of conduct which serve the survival of the group. Those beliefs, rules, and resulting activities form culture. Science aims at objective understanding the world, regardless of its consequences on human emotions, worldview, and social functioning.

Both science and culture were formed by the brain, which is the organ of survival and not of cognition of the world, and it often gives solutions which are at odds with science but pragmatically relevant. The biological purpose of religion is not understanding the universe but securing the group's cohesion necessary for its survival. Science emerged only when it appeared that the objective knowledge of the world may increase fitness.

The conflicts between science and culture emerge when the scientific methods of gathering knowledge offend cultural norms, or when scientific discoveries demonstrate that the foundations of those norms are based on misconceptions.

Biomedical research was particularly often blocked by rulings resulting from cultural norms: today vivisection experiments on humans would be unthinkable. Bioethics, a very modern cultural product, effectively interferes with the progress of science (moratoria on human cloning, restrictions on studying genetically modified organisms and limitation on animal experiments).

Culture is threatened by development of science, resulting in constant downgrading of the position of man from its culturally sanctioned place at the top of material world.

One source of the culture-science conflict is the fact that axioms, methodology, and emotional involvement of humanists in the discussed problems are often completely alien to scientists. Better understanding of the world requires looking for a common language and mutual tolerance of science and culture.

Special symposium: Ethics in Science – II

O-281

THE ETHICAL BASIS OF MULTILATERAL ENVIRONMENTAL AGREEMENTS

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The United Nations Conference on Environment and Development held in Rio de Janeiro in 1992 saw a number of groundbreaking outcomes, such as Agenda 21, a blueprint for a global partnership for sustainable development in the 21st century and the Rio Declaration on Environment and Development with its 27 principles. The Conference was also the birthplace for a series of Multilateral Environmental Agreements (MEAs).

In the chemicals field, the Conference gave impetus for the adoption of the Stockholm Convention on Persistent Organic Pollutants, which entered into force in May 2004. Being the most recent MEA for the management of chemical substances, the underlying values of the Convention embrace contemporary principles in the context of environmental ethics, such as sustainable development, the principle of common but differentiated responsibilities[1], the 'polluter pays' principle[2] or the precautionary principle[3].

We argue that particularly chemists nowadays should have a moral obligation to put into practice the ethical commitments that are inherent to those MEAs. It is thus highly relevant to consider these aspects both as research and educational topics. [4, 5]

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Keywords: *Environmental Ethics; Multilateral Environmental Agreements; Stockholm Convention on Persistent Organic Pollutants; Rio Earth Summit;*

Special symposium: Ethics in Science – II

O-282

PRIMO LEVI: CHEMISTRY, LITERATURE AND ETHICS

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The present talk aims to offer a reading of astory from Primo Levi's book *The PeriodicTable* in a scientific vein, suggesting that chemistry and literature arethe two banks of a same river we call culture. Moreover, the contributionenhances the ethical implications of Primo Levi's lesson. The reader isaccompanied within the story *Cerium*, making him to go into the foldings of the sentences that dealwith scientific laws, phenomena, and discoveries. The purpose is to catch thebond between narration and scientific knowledge, in a setting - that of lager's life - where the tragedy and the existential upset obfuscate and certainly fadeinto the background the technical aspects of which Primo Levi's writing isgreatly soaked in. The narrative thread is not only maintained but it goes toconstitute the essential skeleton onto which the chemical knowledge isexplained rigorously as concerns the content, even though with simplicity inthe form. The aim is to stimulate a critical interpretation and a punctualattention towards those parts, only apparently lacking in literary glamour,that reveal the chemist Primo Levi. The contribution concludes with an outlookof 'memory' that takes cue from another story of the same book, *Carbon*. Thisoriginal view of 'memory' deals only with matter and energy and generates atrue pathos and suggestiveness for people who devote themselves or manifesttheir interest for the scientific rationalization of natural phenomena.

Keywords: *History of science;*

Education in Chemistry – II

O-428

SCHOOL TEACHERS TRAINING

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The training of chemistry teachers at universities is highly diverse in Europe. Regardless the diversity of structures, common content areas of university studies for teachers aiming at a degree for teaching at upper secondary / high level have been identified in a survey carried out in a common project of the network EC2E2N and the division of chemistry education of EuCheMS. Based on this survey and an additional literature research, a framework for chemistry teacher training in Europe has been developed. The framework describes structures to support transition phases between school, university and school again, content areas based on the content descriptions of the EuroBachelor and expected outcomes as skills and abilities both in chemistry and chemistry education.

The talk will present exemplary results form the survey and the literature review and will discuss important feautures of the framework.

Education in Chemistry – II

O-429

ANOTHER TEN IMPORTANT IDEAS FOR UNIVERSITY LECTURERS

I. MACIEJOWSKA[1]

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New lecturers do not always receive appropriate or timely training before undertaking teaching. To address this the first 'Ten important ideas for university lecturers' were presented in the framework of 3rd ECC in Nuremberg.

There were:

Relations with students and within student's group

Start each new group session with a short icebreaker.

Be fair.

Teaching & learning

Be aware/accept/take into account/think about goals/learning outcomes.

Help your students develop their critical skills.

Organise the course/environment friendly for students activity/creativity. Let students do mistakes.

Make sure that lectures are not just "transmit-receive" occasions.

Evaluation

Try your questions out.

Feed back the results to your respondents.

Reflect your own teaching

General

Be prepared and flexible, ready for the question "why?"

In this key-note next ten practical advices[1] for university chemistry teaching staff (especially for those who have recently or will shortly be facing their first class of students) will be presented and discussed. The author will reflect also her own experience of helping diverse groups of doctoral students (future academic teachers) and lecturers in different European countries over last years.[2–4]

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Keywords: *chemistry lecturer; staff development;*

Education in Chemistry – II

O-430

OUTCOMES AND BENEFITS OF INTERNATIONAL COLLABORATION: EVALUATIONS OF THE ACS GLOBAL RESEARCH EXPERIENCES, EXCHANGES, AND TRAINING (GREET) PROGRAM

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The concomitant shifting realities of international collaboration and innovation and the need for problem solving on a global scale provided the rationale for the creation of the American Chemical Society Global Research Experiences, Exchanges and Training (ACS GREET) program. Through GREET, research teams—typically a faculty mentor and a graduate or undergraduate student—receive up to US$11,000 in seed funding to engage a colleague abroad in a new international collaboration.

Over a period of several on-site weeks at an international host institution of their choice, the selected teams initiate a project that enhances their professional skills, knowledge, intercultural competence, and personal networking while advancing the progress of science. The GREET program also facilitates high-risk, high-reward research to be evaluated by enabling U.S. chemical scientist teams and their new partners abroad to collect the feasibility data required to seek additional support; a process that is not always straightforward with current nationally-focused research funding structures.

While the GREET experience is intended as a first step on a long collaborative journey, to date program alumni have already achieved remarkable outcomes that have resulted in: **1**) advances that directly address the grand challenges facing science and society; **2**) the obtainment of large-scale follow-on funding, peer-reviewed publications, and secondary exchanges; and **3**) benefits and enrichments to local communities and home institutions. Quantitative data collected from program alumni and current participants before and after their experience also shows a pronounced impact on their opinions and perceptions of international collaborations.

This paper will provide additional information on the GREET programmatic model and present further details on significant individual, institutional, and global outcomes.

Acknowledgement: *The authors wish to acknowledge ACS and the ACS Committee on International Activities for their support, and the recommendations from former ACS President Joseph Francisco's International Center Taskforce which provided guidance for the program.*

Keywords: *Education; Collaboration; International Exchange; Research funding; Model program;*

Workshop for University Teaching Staff

O-431

WORKSHOP FOR UNIVERSITY TEACHING STAFF

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Feedback and evaluation workshop

In this interactive workshop we will explore the related activities of the *feedback* that university teachers give to their students and the *evaluation* by students of the teaching that they receive. The United Kingdom's National Student Survey will be used as an example of how evaluation takes place on a national scale, and to demonstrate that feedback continues to pose challenges for teaching staff across the range of universities.

The ways in which effective feedback can be given will be considered by asking participants to work on a simple example. They will then be asked to discuss a written case study in which expectations have not been adequately managed, and to comment on a conversation between a group of students in which they discuss the feedback they have received.

The need for university teachers to evaluate their performance will then be considered. The ways in which this can be done through self reflection and seeking information from students, colleagues and external sources will be discussed, including the advantages and disadvantages of each source of information. The need to reflect on such evaluation will be stressed, before deciding whether to act upon it and if so to what extent.

Evaluation was a topic investigated by one of the European Chemistry Thematic Network's working group[1].

The workshop is open to all who are interested in improving their teaching, and opportunity will be provided to compare existing practice within the countries that will be represented.

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TEACHER/TEACHING EVALUATION BY STUDENTS
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Keywords: *chemical education; teaching; feedback; evaluation;*

Environmental Radiochemistry – Fukushima and Chernobyl

O-020

ENVIRONMENTAL EFFECTS OF THE FUKUSHIMA ACCIDENT – COMPARED TO THE CHERNOBYL ACCIDENT

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On 11 March 2011 Japan suffered a large earthquake. The epicentre was just over 180 km from the site of the Fukushima Daiichi nuclear power plant. At the time of the earthquake, three of the site's six nuclear reactor units were operating at power. The reactors were automatically shut down when the earthquake struck. Furthermore, in less than an hour a massive tsunami generated by the earthquake flooded the coast of Fukushima. The damage caused by the flooding resulted in loss of cooling to the reactor units. This led to overheating, hydrogen explosions and a partial melting of the reactor cores. As a consequence, major releases of radioactive material to the environment occurred. These releases were mainly gaseous releases to air, but subsequently there were also liquid releases to the sea through discharge of water used to cool the reactors. The nuclear accident was classified at Level 7, the highest on the International Nuclear and Radiological Event Scale (INES), the same level as for the Chernobyl accident in 1986.

The most significant released nuclides were isotopes of Iodine and Caesium, but a large spectrum of other nuclides was detected, too. Small amounts of radionuclides originating from Fukushima were detected in air samples all over the world. Measured Iodine-131 and Cs-134+137 concentrations in the sea water near the Fukushima Daiichi were also considerable. Radioactive deposition contaminated heavily the nearby land areas of Fukushima Daiichi, and the distribution of contamination levels in other parts of the Fukushima prefecture exhibit significant variation with location. Foodstuffs like milk, vegetables and meat as well as tap water were contaminated soon after the accident in Fukushima but also in neighbouring prefectures. Contamination of the seafood occurred later.

In this presentation, environmental effects of the Fukushima accident will be discussed and compared to the Chernobyl accident.

Keywords: *Environmental chemistry; Radiochemistry;*

Environmental Radiochemistry – Fukushima and Chernobyl

O-021

ESTABLISHING CS-137 AND CS-134 LEVELS IN SEAWATER IN THE PACIFIC OCEAN BETWEEN FUKUSHIMA AND HAWAII

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The Fukushima NPP accident after the March 11, 2011 earthquake and tsunami led to large releases of radioactive contaminants into the ocean. To determine the Pacific Ocean radioactivity spread and levels that might reach Hawaii, seawater samples were collected at eleven stations along the transect from Fukushima to Hawaii from June 21 to July 2, 2011. The surface seawater samples were pumped through a 1-µm filter, acidified to pH 1 with nitric acid, and stable cesium carrier was added.

Cesium seawater monitoring required quick sensitive method allowing to detect ambient levels as well as new releases of ^{137}Cs and ^{134}Cs. We used the AMP-PAN composite absorber, containing ammonium molybdophosphate as an active component and polyacrylonitrile as a binding polymer, and gamma-spectrometry. Samples of about 20 L were passed through 10 mL of AMP-PAN in a glass column by gravity. Dry loaded AMP-PAN was counted using HPGe coaxial detector. Cesium activities calculated from the peak areas at 662 keV for ^{137}Cs and 605 and 796 keV for ^{134}Cs were corrected for decay to the date of collection. Cesium recovery yields determined from carrier concentration difference in seawater before and after the sorption analyzed by ICP-MS ranged from 90 to 97 %.

The cesium radionuclide content in seawater samples taken along the transect from Fukushima to Hawaii ranged from background pre-Fukushima levels (1-2 Bq.m^{-3}) for ^{137}Cs and values bellow the limit of detection (tenths of Bq.m^{-3}) for ^{134}Cs south of the Kuroshio current up to 12 Bq.m^{-3} for ^{137}Cs and 10 Bq.m^{-3} for ^{134}Cs at the transect and southern boundary of the current intersection. These values are far below limits of concern regarding human health, but they give information about the radionuclides pathways in the Pacific Ocean. The results confirm models predicted very little radioactivity spreading south of the Kuroshio current.

Keywords: *cesium; AMP-PAN; seawater; Fukushima;*

Environmental Radiochemistry – Fukushima and Chernobyl

O-022

BEHAVIOR OF RADIOACTIVE CESIUM DURING INCINERATION OF MUNICIPAL WASTES CONTAMINATED BY RADIOACTIVE FALLOUT FROM THE FUKUSHIMA NUCLEAR ACCIDENT

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In Japan, radioactive contamination was widely spread by radioactive fallout from explosions of the Fukushima Dai-ichi Nuclear Plant. Within Kanto and Tohoku regions, therefore, not only soils and plants but also municipal solid wastes and sewage sludges were contaminated. Incineration of those wastes has been performed to reduce their volume and mass since before the accident. Unfortunately, radioactive cesium in their incineration ash was highly concentrated compared with untreated wastes. In this study, the incineration of contaminated municipal solid waste was investigated in terms of the partitioning behavior of radioactive cesium between fly and bottom ashes. The investigation shows that the content of cesium in the fly ash, which is particulate matter in the flue gas, was much higher than that in the bottom ash, which is coarse residue left on the grate of waste incinerators. To understand the difference in the content of cesium between fly and bottom ashes, we tried to calculate the thermodynamic equilibrium of the combustion system using a commercial calculation software (FACTSage). The calculated result indicated that cesium preferred to form cesium chloride (CsCl) gas at the combustion temperature, and partially formed solid aluminosilicate (CsAlSi2O6). We considered that the former was the major cesium component of the fly ash and the latter was that of the bottom ash. This consideration was in a good agreement with the additional examination result on a leaching test of fly and bottom ashes, in which the fly and bottom ashes predominantly contained water-soluble and water-insoluble cesium compounds, respectively. Furthermore, the equilibrium calculation also indicated that the inorganic component of combustion waste affected the chemical composition of incineration ash.

Keywords: *Radioactive cesium; Waste incineration; Contaminated municipal waste; Thermodynamic equilibrium calculation; Radioactive contamination;*

Environmental Radiochemistry – Fukushima and Chernobyl

O-023

IMPORTANCE OF CHEMICAL SPECIATION ON THE MOBILITY OF RADIOCAESIUM IN THE TERRESTRIAL ENVIRONMENT

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Norway was one of the countries most seriously affected by the Chernobyl accident. Radioecological research in Norway after 1986 has emphasized the importance of chemical speciation of the radionuclides for their behaviour in soil, water, and sediments. The mobility of ^{137}Cs in boreal soils of Scandinavia with high organic matter content has shown to be much greater than in the previously studied agricultural soils with high content of mineral matter including clay minerals fixing Cs ions strongly. Thus the uptake of Cs in plants from these soils is much greater than previously experienced, and strongly dependent on the chemistry of the soil solution. Particularly high mobility of ^{137}Cs is observed in southernmost Norway where the soils are more acidified than elsewhere. Results from repeated nationwide surveys of natural surface soils show that the decline of ^{137}Cs is greater in coastal regions than in areas farther inland, probably attributable to much greater deposition of Mg^{2+} and Na^+ in the former areas replacing Cs ions on soil particle surfaces. This effect appears to be particularly strong near the southern coast where deposition of NH_4^+ from transboundary pollution is evident in addition to the marine cations. The effect of precipitation chemistry on the ^{137}Cs mobility is found to decline with time, indicating that the ^{137}Cs cations are gradually moving to sites where they are more strongly bound. Experiments where identical soil columns, containing ^{137}Cs from Chernobyl and freshly added ^{134}Cs, are exposed to precipitation of different quality in amounts corresponding to ten years of deposition, largely confirm the conclusions from the repeated soil surveys.

Environment and Green Chemistry

Environmental Radiochemistry – Environmental studies using radionuclides

O-024

CHEMISTRY ON AEROSOL PARTICLES AND ICE

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Condensed matter – air interactions in the environment became a prominent topic in atmospheric science since the discovery that stratospheric ozone depletion is linked to surface reactions of halogen and nitrogen containing species on aerosol particles and ice. Since then, heterogeneous and multiphase chemistry has developed into an active area of environmental chemistry due to the impact of these processes on the budget of many atmospheric gases, to human health and global climate. Driven by the specific needs of laboratory experiments pertaining to the low partial pressure conditions in the atmosphere, we developed a program based on using the short-lived isotope ^{13}N as a tracer to follow the kinetics of reactions of nitrogen oxides with aerosol particles and ice. An overview of these activities with some of the major recent highlights will be given. While the tracer technique allows detecting sparingly low amounts of reactants or products on aerosol particles or ice, the chemical identification can only be achieved through other analytical methods. To that end, we have recently explored synchrotron based ambient pressure X-ray photoelectron spectroscopy and near edge X-ray absorption fine structure spectroscopy (NEXAFS) techniques as a tool to unravel so far unexplored details from the surface and the interior of aqueous solutions, mineral oxides and ice under environmental conditions. In combination with the tracer technique we have built up powerful tools to tackle current challenges in environmental sciences.

Keywords: *Nitrogen oxides; Isotopic labelling; Atmospheric chemistry; X-ray absorption spectroscopy; Kinetics;*

Environmental Radiochemistry – Environmental studies using radionuclides

O-025

RADIOCARBON DATING OF ICE CORES

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Dating of ice cores from high-alpine glaciers is a non-trivial task. Particularly in the deepest parts of the ice core where thinning of the annual layers does not allow for conventional dating such as annual-layer counting on seasonally varying parameters, other techniques are needed to establish precise age-depth relationships.

Recently we developed, published and thoroughly tested a novel approach to apply radiocarbon dating on alpine ice cores. Independent from the presence of large, organic remnants we use the ubiquitously present carbonaceous aerosol particles in the ice to date the samples, thus allowing a much wider and more continuous application. Carbonaceous particles are extracted from the ice samples via filtration prior to a combustion step where the fractions of organic carbon (OC) and elemental carbon (EC) are separated. By means of the compact radiocarbon accelerator mass spectrometry system MICADAS with a gas ion source gaseous CO_2 samples from the combustion step are directly measured.

The method was applied to ice samples from various glaciated regions from the tropics to the poles and conclusive age information could be given for most of them.Ice cores from the Mongolian Altai, the Bolivian Andes and the Swiss Alps were investigated in detail and ages reaching from 1 000 up to 15 000 years before present (BP) have been obtained, thus demonstrating a good performance of the method on Holocene timescales. Polar samples however, which usually contain rather little carbon amounts have to be interpreted with caution as analytical uncertainties are directly linked to sample size. Nevertheless, also thanks to recent improvements in small scale ^{14}C analysis of gaseous samples (sample size down to 3 μg C) we have a dating tool with great potential for ice core related paleoclimate studies to improve and extend new and existing chronologies.

Keywords: *Radiochemistry; Environmental Chemistry; Analytical Methods; Carbon;*

Environmental Radiochemistry – Environmental studies using radionuclides

O-026

NUCLEAR FOOTPRINT

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The successful exploitation of nuclear fission is a defining event in human history. Originally harnessed for purely military purposes, nuclear energy was next utilized for civilian electrical energy production. The latter has become controversial due to several nuclear industrial mishaps. Of these, the Three Mile Island (1979) and Chernobyl (1986) accidents, and the more recent Fukushima Daiichi event (2011), have dominated the discussion. The consequences of the military use of fission have been largely ignored; the radiation legacy of the Cold War is perceived as a thing of the past. In reality, nuclear materials production activities[1,2] and weapons testing[3] between 1945 and 1998 have introduced more radiation into the biosphere than all civilian mishaps combined.[4] It is estimated that the Chernobyl accident represents less than 5% of the total military environmental radiation burden, and that each of the 2053 nuclear weapons tests by far exceeds either the Three Mile Island or Fukushima accidents.

Misconceptions regarding the relative military and civilian contributions to our collective "nuclear footprint" must be reexamined. There exists a pervasive and fundamental misunderstanding of nuclear and radiation issues by politicians, the media and the general public – that is, by the very people whose thoughts and ideas drive public policy. We can only address this issue with unbiased education. That is the goal of the Nuclear Footprint project.

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Keywords: *Isotopes;*

Environmental Radiochemistry – Speciation of actinides in the environment

O-027

ENVIRONMENTAL APPLICATIONS OF XAFS SPECTROSCOPY

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X-ray absorption fine structure (XAFS) spectroscopy is a powerful tool for the speciation of heavy metals in environmental samples and related model systems. During the past decade an increasing number of experimental stations for XAFS spectroscopy on radioactive samples has become available at different synchrotron radiation facilities worldwide. This lecture will review recent environmental applications of XAFS spectroscopy to fission products and actinides to highlight the impact these studies have on our understanding of the biogeochemical behavior of radiotoxic contaminants such as Tc, U, Np, and Pu. XAFS studies related to the sorption and diffusion of Np in natural clay will be presented in greater detail.

Keywords: *X-ray absorption spectroscopy; Environmental chemistry; Radiochemistry; Actinides;*

Environmental Radiochemistry – Speciation of actinides in the environment

O-028

ACTINIDE AND LANTHANIDE SPECIATION WITH X-RAY SPECTROSCOPY: MICRO- TO NANO- AND OTHER DIMENSIONS

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One of the key safety issues associated with high level nuclear waste disposal is the potential release of radionuclides following water intrusion into a repository, followed by corrosion and leaching of waste forms, subsequent breach of the multi-barrier system and radionuclide transport into the surrounding environment. Predicting, ultimately controlling or prohibiting transport of released radionuclides requires detailed understanding of the physical and chemical factors and processes determinant in their transport. Of central importance is the radionuclide speciation, or its chemical and physical form. Synchrotron-based X-ray techniques are extremely useful speciation methods for such investigations related to the safe disposal of high level nuclear waste. Growing sophistication of these techniques and increased brilliance of modern synchrotron sources is helping surmount challenges in speciation investigations of systems with inherent high chemical and physical heterogeneity including waste forms, containers, back-fill, hostrock and ground water, to name a few. In my presentation I will show results from X-ray spectroscopy studies combined with imaging techniques for actinide speciation in spent fuel models, granite, sediment and colloids. Each example is selected to both illustrate several processes affecting radionuclide mobilization or immobilization and to demonstrate the utility of different state-of-the-art techniques on varying length scales.

Keywords: *XANES/EXAFS; actinide; speciation; X-ray techniques;*

Environmental Radiochemistry – Speciation of actinides in the environment

O-029

URANIUM CHEMISTRY IN CITRIC ACID SOLUTION

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For the long-term safety assessment of radioactive waste disposal sites, detailed knowledge of the actinides's migration behavior as a function of pH, temperature, redox potential of the solution and concentration of complex partners is mandatory. The majority of the studies on the uranium chemistry in the presence of carboxylic acids was performed in the acidic pH range and at room temperature. Thermodynamic data of the complexation of U(IV) and U(VI) by citric acid was given by Hummel.[1] The complexation was comprehensively studied by Bonin[2] and Guenther[3] and the photoreduction by Ohyoshi.[4] However, the mechanistic understanding of the basic interaction processes is very fragmentary.

This study is focused on the mechanism and kinetics of the uranium complexation and redox reactions as a function of carbonate and visible light in citric acid solution. To evaluate the impact of these reaction parameters on the uranium – citric acid – system we used UV-Vis, ATR FT-IR and TRLF spectroscopy. In all systems the uranium citrate complexes were detected as solved species. The variation of reaction parameters strongly influence the complexation and redox reactions. The highest reduction rate could be determinate between pH ~3.5 at anaerobic conditions. Especially the presence of carbonate strongly influenced the mechanism of the redox processes. The uranium is stabilized as U(VI) carbonate complex in the U(VI) – as well as in the U(IV) – citric acid – system. The determination and verification of thermodynamic and kinetic parameters of complexation and redox processes will improve the safety assessment of nuclear waste disposal sites.

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Keywords: *Complexation; Redox processes; Uv-vis; ATR FT-IR;*

Environmental Radiochemistry – Speciation of actinides in the environment

O-030

COMPARATIVE INVESTIGATION OF THE NEPTUNIUM(V) SORPTION ONTO GIBBSITE BY MEANS OF ATR FT-IR SPECTROSCOPY

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The molecular reactions of actinides at the solid-water interface play an important role in the retardation of radionuclides in the environment. Hence, the investigation of the interactions of actinides with metal oxides such as $Al(OH)_3$, $Fe(OOH)_x$, TiO_2, or SiO_2, serving as model phases for more complex, naturally occurring minerals in aqueous solution, becomes essential for the safety assessment in the near and far field of nuclear repositories. In recent years, the sorption behavior of neptunium (Np) onto synthetic and naturally occurring minerals was insufficiently studied. The majority of these studies provide macroscopic results presenting sorption capacities of the substrates and the effect of selective parameters on the sorption behavior. However, for a better understanding of the sorption mechanisms, structural information on a molecular level of the type of surface complex is still needed.

Comprehensive studies using ATR FT-IR spectroscopy have been carried out to investigate the in situ formation of neptunyl(V) surface complexes on aluminum hydroxide, namely gibbsite. This substrate serves as a model phase for more complex mineral systems, e.g. clay minerals. The surface complexation of Np(V) on amorphous and crystalline gibbsite was studied in detail by a multiplicity of experiments in the presence and absence of atmospherically derived carbonate. In the absence of carbonate, one inner-sphere complex is formed on amorphous gibbsite, whereas no sorption occurs on the crystalline gibbsite. In the presence of carbonate and dependent on the crystal structure, different surface species (inner-, outer-sphere and ternary) were derived from the spectra.

Keywords: *Absorption; Radiochemistry;*

Mining and the Environment – Biogeochemical processes governing mining

O-146

SUSTAINABILITY IN METAL MINING FROM THE EXPLORATION, THROUGH EXPLOITATION TO FINAL WASTE MANAGEMENT – THE BIOGEOMETALLURGICAL APPROACH

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Exploitation of sulfidic ore deposits is still an inefficient process forming enormous amount of reactive waste material, which undergoes oxidation and can produce acid mine drainage (AMD), resulting in a threat for water and environment. Additionally, this waste material often still contains other elements or minerals of economic values or hazardous potential, which were not considered during exploitation. This is mainly due to poor mineralogical, geochemical, and microbiological characteriaztion of the material from the start of exploration and during the day-by-day mining operation. In order to improve the eficiency of the exploitation of the ore, but also the low-ore grade material of a ore deposit and minimize environmental impacts, a thorough characterization by advanced mineralogical and geochemical techniques in combination with optimized kinetic tests is needed in order to predict how the different geological units will behave in relation to metal recovery or environmental issues. A new integrated approach combining quantitative mineralogy by QEMSCAN®, with sequential extractions (including Rare Earth Elements) was developped. The data is then used for a high resolution acid-base accounting (ABA) in order to predict if the different materials will produce AMD. Modified kinetic cell tests combined with geomicrobiological studies show the evolution and controling parameters in order to improve recovery for example in a leach operation or inhibit element mobility in case of environmental management strategies. The produced data is then integrated into a biogeometalurgical block-model of the deposit, which permits to designate an optimized extraction process to each block due to its specific mineral assemblage and reactivity in metal realease. This give the oportunity to optimize metal recovery and minimize the environmental impact.

Keywords: *Acid mine drainage; geomicrobiology; biogeometallury; Rare Earth Elements; Sustainability;*

Mining and the Environment – Biogeochemical processes governing mining

O-147

USING BIOPROCESSING TECHNOLOGIES TO REDUCE THE ENVIRONMENTAL IMPACT OF METAL MINING ON THE ENVIRONMENT

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Mining of metal ores has often been viewed as a "necessary evil" in terms of its impact on the environment, and the global demand for metals is projected to continue escalate as the size and aspirations of the human population increases. Among the more significant environmental impacts of mining has are its carbon footprint (energy consumed in comminution and extracting metals), and its legacy of waste materials that give rise to highly polluted waste waters that can be released from mine sites long after they are abandoned. Biotechnologies – some established and some novel – can be used to offset some of these negative aspects, and offer more "environmentally benign" approaches for recovering metals from primary ores and solid and liquid mine wastes. Biomining technologies have been used for almost 50 years to recover copper from otherwise waste ("run of mine") rocks, and more recently for extracting gold, nickel, cobalt and other metals from higher grade (reduced) sulfide ores and mineral concentrates. Bio-processing allows metals to be extracted at much lower temperatures (generally 30–50°C) than conventional pyrometallurgy, and the liquid wastes produced allow pollutants such as arsenic to be more readily contained and stored then when released in smelter gases. Recently, a new approach has been described that uses bacteria to extract metals from oxidized ores, such as nickel laterites, again at low temperatures (30–35°C in the "*Ferredox*" process), thereby greatly expanding the scope of biomining. Microorganisms can also be used to selectively remove metals from acidic waste waters, such as acid mine drainage, as sulfides or oxidized minerals. Acidophilic, sulfidogenic bacteria facilitate the recovery and recycling of base metals, such as copper and zinc, while schwertmannite (a biogenic ferric iron mineral produced from mine waters) has commercial value as a pigment or an absorbent of anionic pollutants.

Keywords: *environmental chemistry; green chemistry; sulfur; water chemistry;*

Mining and the Environment – Biogeochemical processes governing mining

O-148

GEOCHEMICAL AND MINERALOGICAL IMPLICATIONS AT DECOMMISSIONED MINE TAILINGS FOR CHOOSING A REMEDIATION SCHEME

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Mineralogical and geochemical investigations play a key role in choosing remediation scheme for decommissioned mine tailings with advanced sulfide oxidation. Mineralogical characteristics of two abandoned mine tailings in SW Finland were studied using conventional techniques (reflected-light microscopy, scanning electron microscopy, electron microprobe analysis, bulk powder X-ray diffraction) and techniques based on synchrotron radiation (μ-XRF, μ-XAS, and μ-XRD), and geochemical distribution of elements was assessed using a five-step sequential extraction method. Additionally, tailings water chemistry was studied.

The surface layers of both tailings exhibited depletion in sulfides, generation of acid mine drainage and elemental mobilization. Dissolved elements and sulfate were partially retained by adsorption and co-precipitaion in Fe(III)(oxy)hydroxides (goethite and ferrihydrite) and Fe(III)(oxy)hydroxylsulfates (jarosite) at Haveri Au–Cu mine tailings, whereas Fe(III)(oxy)hydroxides (arsenical ferrihydrite) and Fe(III)arsenates (scorodite and kankite) precipitated at Ylöjärvi Cu–W–As tailings. The secondary Fe(III) minerals were particularly abundant in cemented layers, and As, Cu, and Zn were enriched in these layers at Haveri, whereas As, Cu, and Co at Ylöjärvi. The Fe(III) minerals proved to be especially important for As retention, with up to 40–100 % of As in the secondary minerals fraction of the total amount in sequential extractions at Haveri tailings. At Ylöjärvi tailings, the respective amount of As in the secondary minerals fraction was 83–94 % in the highly altered samples.

The results highlighted the importance of Fe(III) minerals in the natural attenuation processes. These phases, stable at oxidized ambient, should not be placed under oxygen deficient conditions to prevent reductive dissolution. Hence, after-care and remediation methods common in closing mine sites (such as capping or raising the water table to prevent oxygen transport for sulfide oxidation) are not applicable in abandoned tailings areas. Other passive treatment methods (*e.g.* passive reactive barrier) should be considered according to the site-specific data evaluation.

Keywords: *Adsorption; Arsenic; Water chemistry;*

Mining and the Environment – Remediation of pollution

O-149

ACID MINE DRAINAGE IN THE IBERIAN PYRITE BELT: SOURCES AND REMEDIATION STRATEGIES

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The Iberian Pyrite Belt (SW Spain and Portugal) contains the highest reserves of pyrite in the world with mining activities dating back to prehistoric times. About one hundred abandoned mine wastes and galleries release a huge acidity and metal load to the Tinto and Odiel rivers. Once the mining activity is over, polluting discharges can remain for centuries with no specific responsible entity. In-situ passive remediation technologies are especially suitable for these orphan sites. The concept is to insert a reactive porous material in the natural flowpath of surface and ground waters, and it is implemented through infiltration ponds and reactive barriers, respectively. Calcium carbonate pea-size gravel is the common alkalinity supplier to neutralize acidity and precipitate metals. These remediation systems have been traditionally implemented in coal mines. However, the acid drainages from the Iberian Pyrite Belt contain metal concentrations one to two orders of magnitude higher than those from coal mines and require special designs to avoid quick clogging or passivation (coating) of the grains of reactive material.

To overcome these problems, a Dispersed Alkaline Substrate (DAS) mixed from fine-grained calcite sand and a coarse inert matrix (wood chips) was developed. The small grains provide a large reactive surface and dissolve almost completely before the growing layer of precipitates passivates the substrate. The high porosity and dispersion of nuclei for precipitation retard clogging. However, calcite dissolution only raises pH to values around 6.5, which is sufficient to precipitate the hydroxides of trivalent metals (Al, Fe), but it is not alkaline enough to remove divalent metals. Magnesium oxide buffers the solution pH between 8.5 and 10. A DAS system replacing calcite with caustic magnesium oxide was tested to be very efficient to remove divalent metals (Zn, Cd, Mn, Cu, Co, Ni, Pb) from the water previously treated with calcite.

Keywords: *acid mine drainage; passive remediation; disperse alkaline substrate; calcite; caustic magnesia;*

Mining and the Environment – Remediation of pollution

O-150

PERFORMANCE OF A BIOLOGICAL PERMEABLE REACTIVE BARRIER FOR IN-SITU REMEDIATION OF ACID MINE DRAINAGE: SUCCESSES AND SHORTCOMINGS

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Goal, Scope and Background. Acid mine drainage (AMD) is a major environmental concern at numerous mining sites worldwide. AMD is characterised by a high acidity and elevated concentrations of heavy metals and sulphate and, because of its negative impact on the subsurface systems, much attention is focused on rehabilitating AMD-contaminated groundwater. Biological Permeable Reactive Barriers (bPRBs) have emerged in the last decades as a promising technology for this purpose.

Objectives. This work aims at reporting the 3-year performance of a bPRB for the bioremediation of an AMD-contaminated groundwater. From a broader perspective, and given the scarce data on full-scale bPRBs within this field, the ultimate goal is to provide insights into such systems and aid design of other future bPRBs.

Methods. Following a throughout investigation of a site seriously affected by AMD, a bPRB was installed at the underlying aquifer. The bPRB was divided into three modules containing different proportions of compost, limestone and zero-valent iron. A network of piezometers upstream, inside and downstream the bPRB was used to monitor changes in groundwater quality by the passage through the bPRB.

Results and Discussion. Overall, the bPRB proved to be effective at neutralizing pH and removing heavy metals from groundwater (removals > 95%). However, shortcomings were also evident. Sulphate was far from being completely depleted, probably due to the poor degradability of compost and to the too short residence time within the bPRB. From a hydraulic perspective, the low permeability of some modules prevented the bPRB from properly intercepting the entire contaminated groundwater plume.

Conclusions. The results demonstrated that bPRBs can be an effective technology for in-situ bioremediation of AMD-impacted aquifers. Considering the expansion of this technology, more data will predictably be generated within the coming years and will provide a good base for better identifying benefits and limitations of this technology.

Keywords: *acidity; biological activity; environmental chemistry; transition metals;*

Mining and the Environment – Remediation of pollution

O-151

THE RED MUD DISASTER OF AJKA IN HUNGARY AND ITS CONSEQUENCES

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The worst and the largest environmental disaster occurred on October 4, 2010 in Hungary, when the wall of a waste reservoir disrupted and a hazardous spill of red sludge burst outside of the territory MAL Hungarian Aluminium Production and Trade Company Limited by Shares.

The caustic sludge flooded three villages and contaminated the rivers and streams including the nearest Stream Torna, which flows through Rivers Marcal and River Rába into the River Danube. The heavy metals contents of soil samples taken from the critical points were investigated as well. Monitoring of particulate matter (PM10) was required in areas affected by red mud especially at settlements situated close to catastrophe site where the particle levels of air were suspected to be high.

The aim of the paper presented the disaster after the intervention and its effects.

Gypsum originating from the neutralization of stack gases of coal-fired power plant was added under controlled conditions and under continuous monitoring at several points along the Stream Torna and River Marcal. In October 2010 the Accredited Water Quality Telemetry System was installed in the direct vicinity of Stream Torna in Devecser. The PM10 concentrations were measured by the Environmental Mobil Laboratory of University of Pannonia.

According to the results the pH level presently is below 8.5 due to the complex impacts of the interventions and natural self-cleaning, good weather and human activities (riverbed cleaning). Introduction of the dry red mud technology was commenced by MAL Co. Ltd. on April 3, 2011. So the water content of red mud sludge was decreased from 80 % to 30 % as a consequence of the modification in technology.

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Keywords: *water chemistry; basicity; Materials science;*

Mining and the Environment – Assessing environmental impacts

O-152

IMPACT OF URANIUM MINES CLOSURE AND ABANDONMENT ON GROUNDWATER QUALITY

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Purpose: The aim of article is to assess the evolving mine water quality of abandoned uranium mines in the Czech Republic. This paper focuses on the changes in mine water quality over time and spatial variability.

Methods: In 2010 systematic monitoring of mine water quality at all available locations of previous uranium exploitation was performed. Gravity flow discharges (mine adits, uncontrolled discharges) or shafts were sampled. Since the mine water quality results from multiple conditions – geology, type of sample, sampling depth, time since mine flooding, the assessment was done taking into account all these conditions. Multivariate analyses were applied in order to identify samples groups based on their similarity. Hydrogeochemical evolution of mine waters was assessed using the Geochemist's Workbench and PHREEQC.

Results: The sampling proved that uranium concentrations in mine waters predominantly did not exceed 0.45 mg/L. In case of discharges from old adits abandoned more than 40 years ago uranium concentrations were below US EPA MCL for uranium in drinking water (0.03 mg/L). Higher concentrations up to 1.23 mg/L of U were found only at active dewatered mine. Concentration of ^{226}Ra varied from 0.03 up to 1.85 Bq/L except for two sites with increased background values due to rock formation (granites). Radium has typically increasing trend after mine abandonment with large variability. Concerning metals, Al, Co and Ni exceeded legislative limits on two sites with low pH waters.

The mine water quality changes with a focus on uranium mobility were described from recently dewatered mines to shafts with maintained water level in order to prevent outflows to surface water and finally to stagnating shafts and discharges from old adits. The results were in good agreement with experience on mine water stratification, its disturbance by pumping or natural water decant and the "first flush" phenomenon after mine flooding.

Keywords: *uranium; environmental chemistry;*

Mining and the Environment – Assessing environmental impacts

O-153

THE IMPACT OF METAL MINING ON SELECTED RIVER SYSTEMS IN ROMANIA

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Base and precious metal mining is one of the human activities with significant impact on the rivers, introducing large quantities of heavy metals and other contaminants into the river drainage. Romania has a long tradition in metal mining, the ore exploitation and processing being now closed, which impose a new perspective on sustainable long-term management of mine waste and mining site rehabilitation, as many such deposits continue to produce acid drainage with adverse effects on the environment.

The paper aims to provide an overview of the most contaminated river systems in Romania, assessing their behavior in time, starting from the year 2000, when two tailings dam failures in Maramures County strongly affected the Tisza-Danube river systems. The study utilizes geochemical data to assess the dispersal of metal contaminants from the mining source along the river systems by assessing metal concentration in several environments: surface and underground water, channel and floodplain sediments and mine tailings. An example of acid mine drainage formation within an active mine tailings dam (e.g. Mialu, Certej catchment) will be given, this being an importance source of mining-related contaminants in the fluvial system. Lead isotopes (^{204}Pb, ^{206}Pb, ^{207}Pb and^{208}Pb) have been utilized as geochemical tracers of the anthropogenic activities in the lower Danube Basin (mainly from Romania, Serbia and Bulgaria) in order to identify the isotopic signature of different ore deposits and to characterize mining affected river catchments, representing important information for the management and remediation practices. Even the metal mining is now closed in Romania, the improperly managed mine deposits continue to introduce large quantities of metal contaminants into the river systems, and thus a robust ecological remediation programme is needed, also considering that several mining sites have proved to be economically viable to be re-opened in the near future.

Mining and the Environment – Assessing environmental impacts

O-154

PAST AND CURRENT METAL AND METALLOID CONTAMINATION FROM ABANDONED MINING SITES IN THE SURFACE WATERS OF THE GARDON RIVER WATERSHED (SOUTHEASTERN FRANCE)

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The Gardon River basin, located in the southeast of the Massif Central (France), drains many disused mine sites. Metal-rich wastes remaining at these sites represent potential sources of metals and metalloids to the Gardon River. Besides post-mining related pollution, current industrial and urban activities may also contribute to metal enrichment. Considering the important cost of remediation efforts, it is important to determine the relative contribution of abandoned mining sites to contaminant loads in a river system.

In this study, metal and metalloid concentrations were determined in water (dissolved and particulate phases) and sediment samples collected during high and low flow conditions throughout the Gardon watershed. Element concentration ratios were used to identify the main contaminant sources. Zinc isotopic composition in suspended particulate matter and sediment samples was also determined in order to evaluate the possible use of Zn isotopes as tracers of anthropogenic contaminations in this context of multiple pollution sources. Current metal contamination status of the Gardon River was compared to historical record. For this, metal and metalloid concentration, element ratios and Zn isotopic composition were determined in flooding layers of a sediment core sampled on the river bank in downstream Gardon River.

The sediment core has recorded an increase of metals and metalloids enrichment from the late 19th century, in association with the beginning of the industrial era. This core also reveals high levels of contamination in 1976 related to the breaking of a tailing dam. Nowadays, some tributaries remain severely impacted by old mining sites and constitute an important input of contaminants to the Gardon River mainly during floods. However, other tributaries impacted by urban and industrial areas are emerging as significant pollution sources for the Gardon River.

Keywords: *Mine-affected river; Metal and metalloid contamination; Zinc isotopy; Sedimentary archive;*

Mining and the Environment – Assessing environmental impacts

O-155

MINE WATER GEOCHEMISTRY AND METAL FLUX IN A MAJOR HISTORIC PB-ZN-F OREFIELD

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Recent studies have shown up to 6% of rivers in England and Wales to be impacted by discharges from abandoned metal mines. Despite the large extent of impacts, there are still many areas where mine water impact assessments are limited by data availability. This study provides an overview of water quality, trace element composition and flux arising from one such area; the Yorkshire Pennine Orefield in the UK. Mine drainage waters across the orefield are charectrised by $Ca–HCO_3–SO_4$ type waters, with moderate mineralization (specific electrical conductance: 160 to 514 µS cm^{-1}) and enrichment of dissolved Zn (≤2003 µg L^{-1}), Ba (≤971 µg L^{-1}), Pb (≤183 µg L^{-1}) and Cd (≤12 µg L^{-1}). The major ion composition of the waters reflects the Carboniferous gritstone and limestone-dominated country rock, the latter of which is heavily karstified in parts of the orefield, while sulphate and trace element enrichment is a product of the oxidation of sphalerite, galena and barite mineralization in particular. Many of the discharges and receiving streams are close to saturation, or supersaturated with respect to calcite, with secondary instream carbonates and biofilms likely to be crucial in controlling downstream mobility of divalent metals. The overall flux of metals released from 26 monitored adit discharges is estimated from baseflow measurements to be in the region of 2890kg Zn year^{-1}, 160kg Pb year^{-1} and 16kg Cd year^{-1}. These figures are put in context with national inventories of metal release and the impacts of the discharges are assessed with regard to the physico-chemical nature of receiving watercourses.

Keywords: *mine water; zinc; lead; cadmium; pollution;*

Mining and the Environment – Assessing environmental impacts

O-156

HYDROCHEMICAL CHARACTERISTICS OF MINE WATERS FROM ABANDONED MINES IN SERBIA AND THEIR IMPACT ON THE ENVIRONMENT

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Research and exploitation of gold, bismuth, wolfram, copper, zinc, lead, coal and uranium deposits were very intense in Serbia. Upon completion of the research and exploitation of mineral resources, many mining sites were abandoned, without previous establishing environmental protection measures, from which mine waters have been discharged uncontrollably in surface flows. Research on wide area were conducted to determine the chemical characteristics of mine waters from abandoned mines of various types of ore deposits.

Based on conducted research it was concluded that in cation composition predominates Ca^{2+}, while the most common anions are SO_4^{2-} and HCO_3^-. Statistical analysis of 20 selected samples showed strong correlations between pH value and content of metals (Fe, Mn, Zn, Cu) in mine waters, whereby with decrease of pH value concentrations of these metals increase. Cluster analysis was applied on all analyzed parameters and, as a result, four groups of mine waters were separated. Mine waters were also classified on the basis of parameters that in high concentrations can have harmful effects on the environment (pH, TDS, SO_4^{2-}, Fe, Mn, Zn, Cu, As, Ni). With this approach, in a separate group were abstracted mine waters related to Cu and Pb-Zn deposits, whose composition is the result of AMD (*Acid Mine Drainage*). According to their chemical composition, they are sulfate waters with increased concentrations of total iron, manganese, copper, zinc, arsenic, and other metals. Uncontrolled discharge of these waters directly into surface waters leads to degradation of quality of the latter, which is further influenced by old mine tailings, in which low grade ores are deposited.

Keywords: *water chemistry; environmental chemistry; acidity;*

Mining and the Environment – Assessing environmental impacts

O-157

LEGACY MERCURY IN SOILS AND TREE RINGS IN THE CZECH REPUBLIC

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Metal mining and processing in the central Czech Republic has led to the contamination of surrounding soils and vegetation. Here we studied vertical distribution and Hg speciation in soils to evaluate the extent of contamination and potential Hg mobility in the area. Mercury speciation was determined by thermo-desorption analysis. Results showed that HgS contamination in a former mining area occurs in most surface soil horizons, but contamination of mineral horizons appears to be limited. Mercury concentrations ranged from 8 to 10 $\mu g\ g^{-1}$ in surface soil horizons and from 3 to 9 $\mu g\ g^{-1}$ in the underlying mineral horizons. In soils high impacted by mining approximately 50-80% of total Hg was present as relatively insoluble HgS in all soil horizons. The remaining of total Hg was attributed to adsorbed phases on mineral surfaces. Soils in greater distance from mine shaft contained HgS only in surface horizons, likely deposited as fine particles. Mercury in mineral horizons was present exclusively as Hg(II) weakly-bound to mineral particles.

Mercury in tree rings was investigated to reconstruct past atmospheric pollution in the area. The highest Hg concentrations were found in spruce at HgS smelting contaminated site (up to 15 $ng\ g^{-1}$). In the vicinity of a Pb smelter, Hg concentrations increased from the 1950s to maxima (up to 8.4 $ng\ g^{-1}$) in the 1970s, corresponding with a peak of metallurgical production and smelter emissions. Trees growing at a site between two smelters seem to reflect deposition from both point sources. Results indicated that tree rings may serve as a reliable archive of Hg deposition in areas affected by ore mining and smelting.

Keywords: *mercury; speciation; mining; contamination; geochemical archive;*

Environmental Chemistry – Emerging contaminants, POPs, phototransformation

O-158

HEXABROMOCYCLODODECANE (HBCDD) – A BROMINATED FLAME RETARDANT USED IN POLYSTYRENE INSULATION

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Hexabromocyclododecane (HBCDD or HBCD) is an emerging chemical with POP-properties used mainly as a flame retardant in the very much used polystyrene-based building insulation products (EPS/XPS), and the consumption of HBCDD is increasing. In addition HBCDD is used in electronics as a substitute for banned flame retardants (PBDEs). HBCDD is a lipophilic and persistent organic pollutant which accumulates in natural organisms and magnifies through the food chain, leading to progressively increasing background levels in human tissues and in wildlife, especially of the most stable α-isomer. The extent of this accumulation correlates directly with its ever-more prevalent use. HBCDD has been detected in air, water, soil and sediments in many countries, and it occurs in indoor air and dusts and in building waste. Very high levels have been found especially in aquatic sediments at close-to-point sources, such as industries producing or using the substance. In recent years, background levels have increased significantly. In 2008 The European Chemicals Agency identified HBCDD as 1 of 14 substances of "Very High Concern", and in September 2010 HBCDD was added to REACH's Authorization List. In February 2011 HBCDD was among 6 chemicals added to Annex XIV of the EU REACH Regulation selected to be phased out before August 2015, if authorisation is not granted before. On 5th March 2012 ECHA published information about the content ($>0.1\%$) of the 53 substances of very high concern in consumer articles. ECHA based that info on 203 notifications from companies notifying 18 chemicals in April to December 2011. HBCDD was the second most notified with 30 notification and it was used in articles in the construction and building sectors such as plastic panels for the thermal insulation of buildings. It was also notified in polystyrene foam used for packaging and in the plastic housing of electronic appliances.

Keywords: *environmental chemistry; toxicology;*

Environmental Chemistry – Emerging contaminants, POPs, phototransformation

O-159

ADSORPTION OF ORGANIC COMPONENTS ONO NATURAL PERLITE AND VERMICULITE CLAYS

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Clays are the main components of the mineral fraction of soils. They are effective natural adsorbents due to their particle size and lamellar structure. Numerous works have been done for using clays as adsorbents to remove organic and inorganic components from water. Perlite and vermiculite are the natural clays that used for the adsorption of the components from water.

Perlit is a glassy volcanic rock which is essentially a metastable amorphous aluminum silicate, expands to about 20 times its original volume upon heating within its softening temperature range of 760 to 1090oC. Also, vermiculite is the another natural clay which has 2:1 layer silicate. Vermiculite also expands to 30 times its original volume depending on the presence of combined water. After the expantion process of perlite and vermiculite minerals, they have larger pore sizes and that makes them to have good adsorption capacities.

In this study, modification of natural clay minerals has been studied. For the modification process hexadecyltrimethylammonium bromide (HDTMA), which is a cationic surfactant, and gallic acid have been used. Experiments were run in batch system. Adsorption capacities of perlite and vermiculite minerals and isotherm models have been investigated. Sorption mechanisms of organic components onto perlite and vermiculite minerals are also studied. In the experiments various concentrations (50%–300% of CEC of the clays) of HDTMA and gallic acid have been used. For both perlite and vermiculite samples, adsorption capacity increased with increasing concentration and we found that experimental data were correlated well by the Freundlich isotherm model. Furthermore, isotherm parameters of Langmuir and Freundlich isotherm models were also calculated. Removal percentage of HDTMA on to vermiculite was 99%, while adsorption percentage onto perlite was around 75%. Gallic acid was adsorbed onto vermiculite around 60%, while it was 45% onto perlite surface.

Keywords: *Adsorption; Perlite; Vermiculite; Hexadecyltrimethylammonium bromide; Gallic Acid;*

Environmental Chemistry – Emerging contaminants, POPs, phototransformation

O-160

COMBINED ELECTROCOAGULATION AND ANODIC OXIDATION PROCESSES FOR SANITARY LANDFILL LEACHATE TREATMENT

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The generation of municipal solid waste grows exponentially in urban society as a consequence of population growth, concentration of population in urban centres and new patterns of consumption. Sanitary landfills are the primary method currently used for municipal solid waste disposal in many countries. One of the main problems generated by this common practice is the production of leachate that is a very complex wastewater containing different heavy metals, organic and inorganic compounds, some of them refractory and toxic, which possesses color and odor. There is a great concern about the contamination caused by landfill leachates, mainly because they are particularly difficult to treat. Thus, it is very important to apply reliable and effective treatment technology. In this study, the electrochemical treatment of leachate samples from an intermunicipal sanitary landfill, collected before the biological treatment, was carried out using combined electrocoagulation/anodic oxidation processes.

The samples collected at the leachate treatment plant and those from the electrochemical assays were analyzed by chemical oxygen demand (COD) and biochemical oxygen demand (BOD_5), dissolved solids, total or dissolved organic carbon and UV-Visible absorption spectrophotometric analyses. The electrocoagulation assays were performed with iron consumable anodes, at different initial pH conditions, with and without stirring, at different applied current densities. In the anodic oxidation experiments a boron-doped diamond anode was used and different applied current densities were tested. The influence of the experimental conditions of the electrocoagulation pre-treatment on the anodic oxidation performance was also assessed, as well as the variation of the ratio BOD_5/COD during the electrocoagulation and anodic oxidation processes.

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Keywords: *Landfill leachate; Electrocoagulation; Anodic oxidation; BDD electrode;*

Environmental Chemistry – Emerging contaminants, POPs, phototransformation

O-161

DISTRIBUTION, FATE AND BIOAVAILABILITY OF ANTIDEPRESSANTS AND THEIR METABOLITES IN WASTEWATER EFFLUENTS AND AQUATIC ENVIRONMENT

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Municipal effluents are important source of contaminants including many pharmaceuticals and their metabolites, whose potential impacts on the receiving environment are poorly understood. Substances like anti-depressant, and anti-convulsive drugs, are now being frequently measured in municipal wastewaters. These substances undergo major transformation at the treatment plant and again in the receiving waters, and thus their bioavailability and toxicity may be modified considerably. The influence of different wastewater treatment processes on pharmaceutical products was investigated. Results showed strong evidence that primary treatment and trickling filter/solids contact has limited capacity to remove antidepressants from sewage, while activated sludge, biological aerated filter, and biological nutrient removal processes yielded moderate results (mean removal rates: 30%). Parent compounds were removed to a greater degree than their metabolites. The target antidepressants were also detected in samples taken from effluent receiving waters, but at lower concentrations (0.41 to 69 ng/L). Bioaccumulation in top predator fish that are exposed to effluent dispersion plumes was investigated. Bioaccumulation potential was also investigated in brook trout exposed for 3 months and significant amounts of the antidepressants were found in fish tissue—in decreasing order: liver > brain > muscle. Sertraline and its metabolite desmethylsertraline were the predominant substances observed in most tissues (0.04–10.3 ng g^{-1}). Biological effects on fish brain were observed as Na/K-ATPase activity in brain synaptosomes was significantly correlated with brain tissue concentrations of fluoxetine ($r = -0.57$; $p < 0.03$), desmethylsertraline ($r = -0.84$; $p < 0.001$), and sertraline ($r = -0.82$; $p < 0.001$). To assess the impacts of all these drug residues on the environment and human health, we still need to better understand their chemical and physical transformations occurring at the treatment plant and in the receiving waters.

Keywords: *pharmaceuticals; bioaccumulation; antidepressant; wastewater;*

Environmental Chemistry – Emerging contaminants, POPs, phototransformation

O-162

DYNAMICS OF BIOCIDE AND BIOCIDE METABOLITE CONCENTRATIONS IN STORM WATER IN A RESIDENTIAL CATCHMENT AREA

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In suburban areas biocides may be used in two applications relevant for storm water: protection of facades and urban gardening. Houses are increasingly equipped with thermal insulation to increase the energy efficiency of heating. The plasters of these systems are often equipped with biocides – from these surfaces the respective compounds may be washed off. As rain water run-off is directly discharged into the aquatic environment via separated sewer systems, storm water overflow and rain water infiltration, discharge of storm water run-off needs consideration. Urban gardening agents (herbicidal compounds) may runoff from parking lots, roads, ways etc.

Within this study the storm water run-off in a well described residential catchment area in Silkeborg (Denmark) was analyzed during a long term study in order to investigate the relevance of leaching from "natural" urbanised areas. No new buildings or major fresh treatment were identified in a spatial assessment. The samples were taken as time resolved samples from a separated sewer system, and analysed for a multitude of biocides, e.g. terbutryn, tebuconazole, diuron, carbendazim, octylisothiazolinone, dichloroisothiazolinone, as well as BAM and atrazine. Temporal developments of concentrations and mass-flows are determined. Both concentrations and mass flows were very dynamic with two to three orders of magnitude between peak and background concentrations. The peak concentrations reached up to 1800 ng/L while the mass transports reached up to a few 10000 ng/s or 77 mg/event (e.g. terbutryn, carbendazim). At least two different release mechanisms are obvious for different compounds. One might be connected to first flush events (possibly emissions from newly treated materials from small areas) while others are classical leaching emissions in which the mass transport is directly related to the hydraulic flow.

Keywords: *biocide leaching; facade coating; carbendazim; BAM; storm water;*

Environmental Chemistry – Emerging contaminants, POPs, phototransformation

O-163

ASSESSING THE INDIRECT PHOTOREACTION OF PARTICLE-BOUND POLLUTANTS

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Humic substances (HS) are known to sensitize the photochemical production of reactive oxygen species, such as singlet oxygen ($^1O_2$). $^1O_2$ is highly reactive and has an important role in photodegradation of aquatic pollutants. The relative importance of dissolved organic matter (DOM) and particulate organic matter (POM) is almost certainly dependent on whether the reaction is occurring in the bulk solvent or on the particle. Some studies have shown no difference in $^1O_2$ production upon irradiation of natural samples before and after filtration, using a probe molecule localized in the bulk aqueous phase. In order to better understand the problem, a well-controlled model system was used. Monodisperse particles of known composition containing organic matter were synthesized. $^1O_2$ production rates were compared between DOM and POM samples. $^1O_2$ measurements were performed with two probe molecules that are localized in the bulk of the solvent and in the organic matter microphase: furfuryl alcohol (FFA) and 2-[(1-(3-*tert*-butyldimethylsiloxy)phenyl)-1-methoxy-methylene]tricycle[3.3.1.1]decane (TPMA), respectively. The $^1O_2$ steady state concentrations ($[^1O_2]_{ss}$) detected upon irradiation of POM and DOM solutions, using TPMA as probe molecule, are similar. Those $[^1O_2]_{ss}$ are also significantly higher than the one obtained using FFA as probe molecule (up to four order of magnitude for POM containing solutions). These results confirm the strong dependence of the apparent $[^1O_2]_{ss}$ on the localization of the probe molecule in the system. It also offers evidence of the importance of POM in the indirect photodegradation of hydrophobic pollutants.

Keywords: *Environmental chemistry; Singlet oxygen; Sensitizers; Photolysis;*

Environmental Chemistry – Emerging contaminants, POPs, phototransformation

O-164

KINETIC STUDIES ON THE PHOTO-OXIDATION REACTION OF WATER BY QUINONES

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One way to utilize solar energy uses photochemical reactions oxidizing water (preferably in aqueous medium), then the reduced reaction partner can be used directly or indirectly to produce energy. In the indirect way, the reducing agent reacts with another redox system (*e.g.* carbonates) and reduces it to a form which is finally suitable for energy storage (*e.g.* methanol).

One possibility is to use unsubstituted and/or substituted *para*-benzoquinones (1,4-benzoquinone; a2-methyl-1,4-benzoquinone; 2,6-dimethyl-1,4-benzoquinone; 2,6-dimethoxy-1,4-benzoquinone; 2,6-dichloro-1,4-benzoquinone; 2,5-dichloro-1,4-benzoquinone) as photosensitive compounds. They are readily soluble in water depending on their substituents. When reacted with light, there are two major reaction types occurring in their solutions. The first is formally a disproportionation reaction, which together with water addition, gives hydroquinone and hydroxyquinone, the latest being a highly absorbing species in the Vis wavelength range responsible for the color of the resulting solutions. The second way is a redox reaction with water, where water acts as a reducing agent and gives oxygen gas and hydroquinone. This scheme is valid for simple substituted quinones as well, with different quantum yields and product ratios. p*K* values of the hydroxyquinone products also depend on the substituents and were determined from spectrophotometric titrations.

In a further reaction, the light induced decomposition of the side product hydroxyquinone was also detected.

For the detailed mechanistic studies, a UV-Vis diode array spectrophotometer was used in addition to a specially designed pH-stat pH-potentiometric system in combination with a high intensity UV lamp emitting at 365 nm. These techniques provide the possibility to detect the spectral changes or change of pH as a function of illumination time. CV measurements gave further information about the redox properties of the different quinones to find the best candidate for solar energy utilization.

Keywords: *Photochemistry; Kinetics; Quinones; UV/Vis spectroscopy; Cyclic voltammetry;*

Environmental Chemistry – Emerging contaminants, POPs, phototransformation

O-165

PHOTODEGRADATION OF THALIDOMIDE: IDENTIFICATION OF TRANSFORMATION PRODUCTS BY LC-UV-FL-MS/MS, ASSESSMENT OF BIODEGRADABILITY, CYTOTOXICITY AND MUTAGENICITY

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The presence of pharmaceuticals in the environment has become an important emerging environmental issue. The ecological impacts, possible human health effects, and potential risks associated with releases of pharmaceuticals into the environment have become an increasingly important issue for scientists, the public, and environmental regulators.

In 1998, Thalidomide (TD), notorious for its teratogenicity, was approved by the FDA for the treatment of erythema nodusum leprosum associated with leprosy. Recently, TD is a promising drug in the treatment of a number of cancers and inflammatory diseases.[1] Consequently, a potential increased influx of TD into the environment makes it imperative to assess the fate of TD and its possible degradation products. In this study the behavior of TD was monitored during photoirradiation using medium-pressure Hg-lamp in different reactors. Biodegradation of TD and its phototreaction products was assessed in Closed Bottle Test (CBT). Cytotoxicity and Mutagenicity of TD and photodegradation products (after 2, 4, 8, 16 and 32 min of irradiation) were done with *Salmonella typhimurium* strains TA 98, and TA 100 in the Ames MPF with and without metabolic activation.

The primary elimination of TD was monitored and structures of photodegradation products (PPs) were assessed by LC-UV-FL-MS/MS. New PPs were formed of which two were isomers of TD with the same molecular mass. Further, TD and its PPs were neither readily biodegradable in CBT nor exhibited cytotoxic nor mutagenic activities at the highest tested concentration of 50 mg/L.

Additional toxicity studies with other endpoints (bacterial toxicity, genotoxicity) and structure-activity relationship will be applied for the further characterization of the environmental and human risks connected with the presence TD and its PPs in the environment.

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Keywords: *Pharmaceuticals; Environment; Transformation products; UV treatment; Toxicity;*

Environmental Chemistry – Metals, transformation

O-283

TESTING PREDICTIVE CAPABILITIES OF SPECIATION MODELS IN FRESHWATERS USING A LABORATORY-ASSAY APPROACH

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A potential problem of speciation models used for predicting binding of metals to natural organic matter is that they are parameterised using extracted humic and fulvic acid (HA and FA). A series of 7 standardised laboratory assays were developed to measure the binding characteristics of Cu to dissolved organic matter (DOM) rather than extracted HA and FA. To obtain DOM, ~80 L samples (per site) of freshwater were collected from two headwater streams in the North Pennines, England, filtered and cleaned from major cations by ion–exchange. The DOM was concentrated using rotary evaporation to reduce the sample volume to ~500 cm^3. Quality control standard solutions of Suwannee River HA and FA were also prepared. The free Cu^{2+} ion activity in solution was determined using ion–selective electrode (ISE). The lower detection limit on the calibration curve of the Cu–ISE was extended from pCu of ~7.0 to ~14 by complexometric titration with ethylenediamine. To maintain an extended detection window of Cu, the ratio [DOM]: [Cu_{total}] was varied between 62 and 3100 while maintaining the ionic strength constant. The free ion activities in solutions were calculated using WHAM 7 and NICA–Donnan speciation models and compared to those obtained from the laboratory assays. For most of the assays the difference between experimental data and WHAM predictions for both isolated DOM and FA and HA was < 0.7 pCu units. NICA–Donnan and WHAM model predictions agreed within 0.5 pCu units. A systematic increase in the activities of Cu^{2+} was observed in solutions at pH 6.0 following the addition of Ca, Zn and Ni. This was attributed to metal competition at the HA or FA sites. As expected this competition effect was negligible in more acidic solutions. More waters need to be tested, but this study suggests that paremeterisation of models using extracted FA and HA is appropriate.

Keywords: *Dissolved Organic Matter; Ion selective electrode; Freshwater; WHAM model; Chemical Speciation;*

Environmental Chemistry – Metals, transformation

O-284

TASK SPECIFIC IONIC LIQUIDS SYNTHESIS: APPLICATION TO METAL IONS EXTRACTION

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Our work aims to design cationic organic chelating synthons derived from vegetal or animal renewable resources (betaine, glycine or alanine), which can generate original task specific ionic liquids by association with an inorganic anion. These ionic liquids (ILs) are used in order to develop process for pollution remediation.

The cationic synthons, obtained in the form of bromide salts, can generate ionic liquids by metathesis reactions in the presence of the desired anionic salt [BF_4^-, PF_6^-, NO_3^-, $(NC)_2N^-$ (Dca), ClO_4^- and $(CF_3SO_2)_2N$- (NTf_2)]. A series of ionic liquids (ILs) are isolated and characterized by various physicochemical methods (elemental analysis, ^1H and ^{13}C NMR, IR, DSC, viscosity, Karl Fischer titration, crystal XRD).

The extraction of the different metal cations (Cu^{2+}, Ni^{2+} and Pb^{2+}) in aqueous solution by ionic liquids synthesized was performed. The extraction yields, determined by the measurements of the residual metal concentration in aqueous solution, depend not only the length of the alkyl chain appending to the ammonium nitrogen but also on the nature of the associated anion. The most promising results are obtained with ILs whose anion has a chelating ability. The mechanism of metal transfer has been studied and was related to the hydrophobicity of the cationic synthon. Increasing the hydrophobicity of the cationic synthon leads to an increase of extraction yield, thus limiting ion-exchange (transfer of the cation of LI in the aqueous phase) and promoting ion pairing extraction.

Keywords: *Ionic liquids; Ion pairs; Amino acids; Ion exchange; Transition metals;*

Environmental Chemistry – Metals, transformation

O-285

CORK APPLICATION FOR CLEANING METAL CONTAMINATED WATERS

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Metals have become of utmost importance due to our planet's increasing populations and their requirements for natural resources and metals-based goods. The continuous demand for metals has originated metal rich wastewaters and metal contamination problems all over the world. Today, metal contamination has accomplished high visibility and is garnering public concern, since population is less and less tolerant of any risks to their health, safety and quality of life. The impacts that metal contamination has on both public health and ecosystems have forced the regulatory entities to the drive for strict environmental standards and reduction in metal releases and discharges. All over the world, industries are forced to reduce the metal contents in industrial waters to limit levels. Activated carbon is one of the most used sorbent to remove metals from waters, but due to its expensive cost, waste based sorbents have been emerging as a low cost alternative.

Cork stoppers are an abundant waste from households and restaurant units. They are composed mostly by natural cork, and its main polymeric components are suberin, lignin and polysaccharides. Their chemical groups are the main responsible for their capacity to uptake metals. In this study the efficiency of this biomass to uptake Hg, Cd and Pb from different types of water have been studied in batch stirred vessels at room temperature.

Cork have shown higher appetence to remove Hg(II) and Pb(II), achieving removal percentages as higher as 95%.The sorption process was studied under the effects of competing ions and organic matter content, and it is well described by well-known kinetics models. This study suggests that this waste based sorbent may be effectively used to reduce metal content in low and moderate contaminated waters.

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Keywords: *Metals; Cork; Sorption; Competing ions; Organic matter;*

Environmental Chemistry – Metals, transformation

O-286

REDUCTION OF SELENITE TO ELEMENTAL RED SELENIUM BY THE RHIZOBACTERIUM AZOSPIRILLUM BRASILENSE

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Bacteria of the genus *Azospirillum* which form associative symbioses with many higher plants are among the most studied plant-growth-promoting rhizobacteria (PGPR). As the rhizosphere is the common natural habitat of azospirilla, they have high resistance and adaptability to different unfavourable environmental conditions: starvation, drought, etc. Selenium is a trace element which is required for all organisms but becomes toxic at higher concentrations.

We have studied the impact of selenium(IV), SeO_3^{2-}, on the bacterial species *Azospirillum brasilense* (strains Sp7, Sp245, Cd). Concentrations of 0.5–1 mM Na_2SeO_3 completely inhibited the growth of all the strains at the end of the logarithmic phase of growth (18 h) in the liquid medium. However, bacterial growth and a red staining of the culture medium was observed upon further cultivation (stationary phase of growth, from 66 h) at the same concentrations. The red color of colonies was also observed on solid medium in the presence of selenite up to 1 mM.

Using TEM, the presence of intracellular electron-dense spherical nanoparticles (50–400 nm) was shown. X-ray fluorescence revealed a significant accumulation of selenium by bacterial cells. Electron energy loss spectroscopy (EELS) was used to create an elemental map of selenium. The results obtained suggest the electron-dense nanospheres generally found inside the cell to be elemental selenium.

A possible mechanism for the Se^{IV}–>Se^0 reduction involves the inclusion of SeO_3^{2-} in the already existing denitrification process well studied for *Azospirillum*, and may not be due solely to Se^{IV} detoxification.

This is the first report on the ability of *Azospirillum* to reduce selenite to Se^0. The results obtained show that these PGPR may be suitable for bioremediation of selenite-contaminated environments. The ability of *Azospirillum* to synthesize Se nanoparticles can also be of interest to nanobiotechnology.

Keywords: *Biotransformations; Green chemistry; Selenium; Reduction; Nanoparticles;*

Environmental Chemistry – Metals, transformation

O-287

HYDRODEFLUORINATION AND HYDROGENATION OF POLYFLUORINATED BENZENES UNDER MILD AQUEOUS CONDITIONS

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Fluorinated organic compounds are increasingly used and important emerging pollutants. Due to their growing use, release to the environment is expected. In the environment, they are expected to be rather persistent, as fluorinated compounds show increased stability and lipophilicity compared to their non-fluorinated counterparts. Current approaches to C-F bond cleavage either use harsh conditions or homogeneous complexes that are not suitable for use in water or environmental matrices. In this work, we have developed a simple heterogeneous rhodium-based catalytic system for complete hydrodefluorination and hydrogenation of polyfluorinated benzenes with molecular hydrogen under mild aqueous conditions. Degradation kinetics, product and intermediate distributions, as well as data on catalyst–fluoroaromatic interactions will be presented, with a focus on their implications for the underlying reaction mechanisms involved.

Keywords: *environmental chemistry; heterogeneous catalysis; fluorine; reaction mechanisms; rhodium;*

Green Chemistry – I

O-288

THE CLIMATE AND ENERGY POLICY OF THE EUROPEAN UNION: CHALLENGES FOR GREEN CHEMISTRY

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A key element of the EU efforts to promote sustainable development is its "Integrated Climate and Energy Policy", providing for substantial reductions of the green house gas emissions in the EU with a reduction of the consumption of natural resources and a lowering of air pollution as co-benefits. This is a first step towards a conceived massive global effort to limit global warming to 2 degrees, which would correspond to reducing the green house gas emissions globally by 50 % till the year 2050.

New "sustainable and green" technologies have to be developed and implemented. Key development areas refer to new efficient transport systems, houses and consumer devices, renewable energies, carbon sequestration and storage and new energy carriers providing a huge challenge for many scientific disciplines. This lecture aims at presenting key elements of this challenge for "green chemistry", which can be seen as the molecular science of sustainable development.

Green Chemistry – I

O-289

ENERGY CONVERSION EFFICIENCY OF A DIESEL POWER GENERATOR FUELLED WITH ETHANOL-BIODIESEL-DIESEL OIL BLENDS

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This work presents a study on fuel consumption and fuel conversion efficiency of a diesel power generator fuelled with blends of biodiesel, ethanol and diesel oil. Experiments were carried out on the engine fuelled with blends of 5 % (B5), 10 % (B10), 20 % (B20) and 50 % (B50) of soybean biodiesel in diesel oil. In addition, anhydrous ethanol was used as an additive to B20 blend at the concentrations of 2 % (B20E2) and 5 % (B20E5). The engine load was varied from 0 kW to 37.5 kW. The results showed that engine fuel consumption is increased as biodiesel and ethanol concentrations are increased in the fuel. However, the use of ethanol as an additive improves engine fuel conversion efficiency.

Keywords: *Fatty acids; Alcohols; Biomass; Energy Conversion; Renewable Resources;*

Green Chemistry – I

O-290

MESOSTRUCTURED Y ZEOLITE AS SUPERIOR FCC CATALYST—FROM LAB TO REFINERY

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Y zeolite with well-controlled intracrystalline mesoporosity is prepared by a post-synthetic surfactant-templating approach. The mesostructured Y zeolite maintains good crystallinity, excellent hydrothermal stability, and strong acidity, which are critical features for catalysis (e.g. Fluid Catalytic Cracking of petroleum). FCC catalysts made from the mesostructured Y zeolite show much improved product selectivity, i.e. significantly more desirable transportation fuels (gasoline and diesel) and less undesirable products (coke and bottoms) compared to conventional zeolite catalysts, which can be attributed to the improved diffusion of reactants and products in and out of the micropores through the intracrystalline mesopores.

Keywords: *zeolites; mesoporous materials; catalyst; structure-acidity relationship; cracking;*

Green Chemistry – II

O-291

GREEN ENERGETIC MATERIALS

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Oxydation of 1,1-dimethylhydrazine using our recently patented method led to the formation of (*E*)-1,1,4,4-tetramethyl-2-tetrazene (**1**) in high yields and purities. Compound **1** was oxidized with potassium permanganate to form functionalized formyl 2-tetrazenes (*E*)-1-formyl-1,4,4-trimethyl-2-tetrazene (**2**) and (*E*)-1,4-diformyl-1,4-dimethyl-2-tetrazene (**3**). Additionally, compound **1** underwent oxidative addition with chloramine ($Cl–NH_2$) to form the (*E*)-1-aminomethylidene-1,4,4-trimethyl-2-tetrazenium cation (TAT^+) as its chloride salt (**4**). Metathesis reactions of salt **4** with energetic anion transfer reagents led to the formation of ionic compounds based on the TAT^+ cation and the following anions: nitrate (**5**), perchlorate (**6**), 5,5?-azobistetrazolate (**7***$6H_2O$), picrate (**8**) and azide (**9**). All materials described in this work were characterized by analytical (elemental analysis and mass spectrometry) and spectroscopic (multinuclear NMR spectroscopy: ^1H, ^{13}C and ^{15}N NMR and vibrational spectroscopy: infrared and Raman) methods and the solid state structures of compounds **2**, **3**, **4**, **5**, **6**, **7***$6H_2O$ and **8** were determined by low temperature X-ray crystallography. Additionally, we computed the natural bond orbital charges of compounds **2** and **3** and of the TAT^+ cation (B3LYP method). Furthermore, we used preliminary energetic testing to gain insight into the sensitivities of all the materials in this work towards impact and friction and we assessed their thermal stability by differential scanning calorimetry (DSC) measurements. Additionally, the heats of formation of the energetic materials were computed using quantum mechanical methods (CBS-4M) and these values were used to determine the detonation parameters (pressure and velocity) and specific impulses for the pure compounds and for their formulations with an oxidizer. Lastly, we calculated the expected decomposition gases of the pure compounds as well as those of the mixtures with an oxidizer. Based on our studies, the new compounds are of interest as a new type of less sensitive and more environmentally friendly energetic materials.

Keywords: *Ion exchange; X-ray diffraction; NMR spectroscopy; Ab initio calculations; Azo Compounds;*

Green Chemistry – II

O-292

ONE-POT SYNTHETIC PROCESSES BY BETA-NITROACRYLATES: PREPARATION OF PENTASUBSTITUTED ANILINES

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The synthesis of complex molecules is traditionally performed by a sequence of separate steps, each of which requires its own conditions, reagents, solvent, and catalyst. After each reaction is complete, the solvent and the waste products are removed and discardered, and the intermediate product is separated and purified. Environmental and economic pressure are now forcing the chemical community to search for more efficient ways of performing chemical transformations. These issue can be addressed by the development of new synthetic methods which, by bringing togherer simple components, can generate complex structures in one-pot, in much the same way as occurs in nature.[1] In this contest, β-nitroacrylates have demonstarted to be a key starting material for the one-pot synthesis of a variety of fine chemicals, such as dihydroquinoxalinones,[2] benzoxazinones,[3] a,β-unsaturated esters,[4] furans,[5] indoles[6] and pyrroles.[] Following our studies on the reactivity of β-nitroacrylates, we have now found that their reaction with ylidene malonitriles, under basic conditions, affords the one-pot synthesis of penta-substituted, densely functionalized anilines in satisfactory to good overall yields.

Reaction conditions and results will be reported.

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Green Chemistry – II

O-293

KEEPING HIGH SURACE AREA OF CATALYTIC SUPPORTS AT HIGH TEMPERATURE WITH FECRAL METALLIC FOAM

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Conventional catalyst supports made of ceramic materials have problem such as low thermal conductivity and low mechanical shock resistance. In contrast, metallic catalyst supports have superior thermal and mechanical properties over ceramic supports. Although metallic supports have many advantages over ceramic supports as mentioned above, adhesion of coated oxide carrier layer to metallic support surface is weak due to the difference of the respective thermal expansion coefficients.

In this study, we tried porous FeCrAl metallic foam as a support in order to improve those shortcomings of metallic supports mentioned above. γ-Al_2O_3 powder was used as oxide carrier for active catalytic materials. γ-Al_2O_3 powder in distilled water was ground by attrition milling. FeCrAl foam was dipped in the γ-Al_2O_3 slurry from milling. BET, Scanning electron microscopy, and X-ray diffraction were used to characterize our γ-Al_2O_3 carrier/support complexs. In order to investigate the adhesion strength of the γ-Al_2O_3 powder particles to FeCrAl foams, the washcoated metallic foams went through 1200 cyclic thermal shock tests. Each cycle was composed of 1 minute hold at 700degree, and 5 minutes of cooling from 700degree to RT. In order to investigate catalytic activity of the sample, Rh nanoparticles were impregnated in the γ-Al_2O_3 carrier particles. Those Rh-impregnated carrier/support complexs were put into a micro reactor and partial oxidation of DME was carried out in the reactor. Hydrogen yield from the partial oxidation of DME was measured by gas chromatography. In order to compare catalytic efficiency of our FeCrAl foams to that of conventional spherical γ-Al_2O_3 supports, we also prepared Rh-impregnated spherical γ-Al_2O_3 supports and put them in a conventional pack-bed reactor. In the reactor, we measured hydrogen yield from the same reaction mentioned above and compared the results with those from our FeCrAl foams. Our carrier/support complex showed better efficiency than the conventional pack-bed type catalyst.

Keywords: *metal foam; catalyst support; adhesion; washcoat; FeCrAl;*

Green Chemistry – II

O-294

DESIGNING GREENER PLASTICIZERS: INFLUENCE OF GEOMETRY OF CENTRAL GROUP AND SIDE CHAINS

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Plasticizers are important additives for brittle polymers such as poly(vinyl chloride) (PVC). Their addition lowers the glass transition temperature (Tg) making the blends soft and flexible. Because plasticizers are not bound to the polymer matrix, they slowly leach out of the blend into the environment. Many studies have shown di (2-ethylhexyl phthalate) (DEHP) and some of its toxic stable metabolites such as its monoester (MEHP) to be ubiquitous environmental contaminants due to their slow breakdown by soil bacteria. This has led to efforts to design new, “green” plasticizers.

Small diester molecules that resemble DEHP were formed from maleic or succinic acid and esterified with alcohols ranging from ethanol to n-octanol and 2-ethyl hexanol were prepared and tested for their plasticizer properties such as reduction of Tg and tensile strength in blends with PVC. To assess their biodegradability, the compounds were exposed to the common soil bacterium *Rhodococcus rhodocrous* to determine hydrolysis rates and metabolite buildup.

Studies with 2-ethylhexyl diesters showed the importance of the geometry of the central structure in diester plasticizers on biodegradation. When the two esters were in a *cis*-position to one another (maleate), the hydrolysis step of the diester was hindered, while for the saturated succinate, which was free to rotate about the intervening bond, was quickly hydrolysed. Also, no buildup of monoester could be observed for the succinate. Both compounds showed comparable plasticizer properties to DEHP.

On this basis, further studies were undertaken with linear succinate compounds in order to avoid the production of a known toxic metabolite (2-ethyl hexanoic acid). Plasticizer properties were similar to the branched compounds and improved with the overall length of the diester. Hydrolysis rates increased when no branching was present, and were inversely proportional to chain length. The data suggest these small diester molecules are green plasticizers.

Keywords: *Green Chemistry; Environmental Chemistry; Polymers;*

Green Chemistry – II

O-295

BALL MILLING: AN EMERGING TOOL FOR ORGANIC SYNTHESIS

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Over the last two decades a major trend in the field of Organic Chemistry could be observed: environmentally friendly processes using safer reagents, generating fewer side products, as well as a decreased utilization of solvents are en vogue. Taking advantage of this general trend, the performance of reactions under ball milling conditions in the absence of solvents is an increasing field of research, resulting in various publications covering this topic from synthetic point of view, not only dedicated to organic but also to inorganic chemistry as well as to materials and polymer science.

Due to the high energy density during ball milling, reaction times can often be kept short comparable to typical experimental procedures with radiation based energy entry (thermal or dielectric heating). System inherent high mixing efficiency allowed for efficient mixing of lipophilic and hydrophilic compounds without the need for employment of phase transfer reagents or similar additives used in solvent-based processes. Furthermore, continuous particle refinement accounts for the formation of small crystallites with high defect concentration, thus high chemical reactivity. Improving the reactivity of solid materials due to comminution in combination with reduction of mass transport limitations leads to high reactivity of substrates in the solid state allowing several reactions, sometimes with unique selectivity. Using model reactions from different fields of research like cross-coupling, selective oxidation, or cycloaddition the advantages and disadvantages of this technique compared to other methods of energy entry will be demonstrated with regard to feasibility, energy efficiency, and scale-up potential.

Overall results showed that the performance of reactions in ball mills is often beneficial over classical experimental procedures. Reduced reaction times, reduction of solvent utilization, and the suppression of side reactions result in increased yields of the target products and an improved overall energy efficiency and mass intensity.

Keywords: *solvent-free synthesis; solid-state chemistry; metal catalyzed reactions; green chemistry; process intensification;*

Green Chemistry – II

O-296

FABRICATION OF HIERARCHICALLY STRUCTURED ZNO PHOTOANODES FOR HIGHLY EFFICIENT DYE SENSITIZED SOLAR CELLS

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ZnO photoanodes are recently applied as promising alternatives to traditional TiO_2 in dye sensitized solar cells (DSCs). We report hierarchically structured ZnO films as photoanodes in DSCs for the enhancement of photoconversion efficiency, based on three main concepts: (**i**) high optical density of the sensitized layer, allowing complete light absorption in the spectral range of the dye; (**ii**) high light scattering of the absorbing layer, in order to both enhance the residence time of light inside the sensitized film and improve light absorption; (**iii**) inhibition of back reaction. The films are prepared by the simple, cheap and large area scalable spray pyrolysis method and are composed of polydispersed ZnO aggregates consisting of nanosized crystallites. The aggregates are submicrometer-sized and can act as efficient light scattering centers, while the nanoparticles deliver the mesoporous structure and the high specific surface area needed for high dye loading. Additionally, a ZnO compact buffer layer is formed between the conducting substrate and the layer composed of polydispersed aggregates. Such a layer efficiently acts as a blocking layer for the back reaction between the conducting glass at the anode and the electrolyte, preventing electron recombination and improving the functional properties of the cells. Optimized structure led to high light absorption, efficient electron transport and collection, inhibition of back reaction electron recombination, and resulted in unprecedented overall photoconversion efficiency up to 7.4% [1], which is higher than 6.58% for ZnO nanoparticles [2] and 5.4% for hierarchically structured ZnO without blocking layer.[3, 4]

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Keywords: *third generation photovoltaics; hierarchically assembled ZnO; spray deposition;*

Green Chemistry – III

O-297

THE CELLULOSIC SUGAR PLATFORM: SUSTAINABLE BIOFUELS AND GREEN CHEMICALS

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Facing limited fossil resources and rising and fluctuating oil prices, the challenge of this century will be the exploitation of alternative resources to secure growth and quality of life for an ever growing population. Glucose and other sugars are nature's building blocks. The conversion of sugars offers new alternative routes to biobased chemicals and biofuels independent from fossil-based production and with substantial savings in CO_2 emissions.

Therefore, the concept of the biorefinery will become more and more important. Efficient use of resources and energy is essential to secure sustainability as well as economic viability. In particular, second generation products that are based on cellulosic plant components, as for instance wheat straw, corn stover or bagasse, show a significantly improved energy balance and reduce the competition to food production and for arable land.

The presentation will analyze the potential of sugars as a platform for renewable, biobased chemicals. It will furthermore explore technologies and concepts for wholly integrated, 2nd generation biorefineries. The development of economically competitive system solutions for biofuels and biorefineries is of important strategic interest for Süd-Chemie, a member of the Clariant Group. Süd-Chemie's sunliquid® process uses lignocellulosic feedstock such as agricultural residues for the production of cellulosic ethanol and matches the ambitious targets for economically and ecologically sustainable production and greenhouse gas reduction. It was developed using an integrated design concept. Highly optimized, feedstock and process specific biocatalysts and microorganisms ensure a highly efficient process with improved yields and feedstock-driven production costs. Integrated, on-site enzyme production further reduces production costs substantially and assures independence from external suppliers. In July 2011 construction started on a demonstration plant with an annual ethanol output of 1,000 tons. The plant will demonstrate the economic competitiveness to first generation processes and constitutes the last step from laboratory to commercial production. Additionally, the technology opens up a pathway to a second generation sugar platform to ultimately produce green chemicals for a wide range of applications, e.g. organic acids, alcohols, furanics, green solvents and other specialty and bulk chemicals which can be further converted into biobased plastics and polymers.

Green Chemistry – III

O-298

BAEYER-VILLIGER OXIDATIONS WITH IONIC LIQUIDS INTERCALATION COMPOUNDS INTO LAYERED ZIRCONIUM PHOSPHATES

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In the last decades, the use of metal phosphates and ionic liquids in various catalysis reactions received considerable attention.[1–3] However, in contrast to the behaviour of metal phosphates, the separation of ionic liquids from the reactants and products is, frequently, a difficult process. This drawback may be avoided if the ionic liquids are intercalated into suitable materials, such as, α- and γ-zirconium phosphates.[3]

The oxidation of *p*-methoxybenzaldehyde, *o*-methoxybenzaldehyde and 2,4,6-trimethylbenzaldehyde is a very useful reaction, since its products are important starting materials for the production of fine chemicals used in medicine, cosmetics and perfumery.

In our laboratory, their oxidation was performed by hydrogen peroxide catalysed by 1-ethyl-3-methylimidazolium chloride (C_2mim)Cl and 1-hexyl-3-methylimidazolium chloride (C_6mim)Cl intercalated into α- and γ-zirconium phosphates (α- and γ-ZrP),**without solvent** and **in acetic acid** at 60 °C. The molar ratio between the substrate and the oxidant was 1:4. The reaction mixtures were analysed after 3 and 6 hours of reaction by GC and GC/MS chromatography.

The best results, when compared with the blank reaction, were achieved with α-ZrP[C_6mim]Cl, α-ZrP[C_2mim]Cl and γ-ZrP[C_2mim]Cl after **3 hours** of reaction **without solvent**. Good results have also been obtained after 6 hours of reaction and acetic acid. These catalysts have basic properties, so, we suggest that their structure can play a decisive role in the conversion of the 2,4,6-trimethylphenyl, *p*-methoxyphenyl and *o*-methoxyphenyl formates into the respective phenols since the hydrolysis of formates in basic media is irreversible.

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Keywords: *Heterogeneous catalysis; Oxidations; Layered compounds; Intercalations;*

Green Chemistry – III

O-299

NEW CHITOSAN BASED CATALYSTS FOR AZIDE-ALKYNE HUISGEN'S [1,3-DIPOLAR] CYCLOADDITION REACTION

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Chitosan is particularly attractive for application in catalysis in regard to the presence of amino groups and its insolubility in organic solvent. The capacity of chitosan for metal chelation can be strongly increased by the introduction of a ligand. The most straightforward route to functionalizing primary amine containing materials is the reaction with an aldehyde to form an imine (Schiff base formation). Chitosan was functionalized with 11 different ligands and Cu(I) was complexated.

Solids were dried under CO_2 supercritical conditions in order to afford high surface area materials.[1] We evaluated the putative catalytic activity of the solids for the azide-alkyne Huisgens [3+2] cycloaddition reaction under a panel of reaction conditions,. The reaction was monitored by a simple fluorescence measurement of the corresponding triazole producted with a coumarin-based fluorogenic probe. One system appeared more active than the homogeneous system itself, and displayed particularly high efficiency, with only 0.1 mol catalyst.[2] This result was confirmed by kinetic experiments and by a series of experiments conducted at the mmole scale on a target reaction.

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Keywords: *Click chemistry; natural product; green chemistry;*

Green Chemistry – III

O-300

SURFACTANT EFFECTS ON CRYSTAL GROWTH OF CLATHRATE HYDRATE AT INTERFACE BETWEEN WATER

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This paper reports visual observations of the effect of surfactants on the clathrate hydrate crystal growth at the interface of water and cyclopentane. Recently, surfactants are used in gas pipeline to prevent the hydrate agglomeration which causes flow channel blockage. On the other hand, surfactants have the effect of promotion of hydrate formation. These two effects are apparently contradictory and the physical mechanism of the surfactant effects is unknown. Surfactants used in the present study are sorbitan monooleate (Span80), polypropylene glycol (PPG), and naphthenic acid. These were used at the concentration of 1000 ppm and 10000 ppm. These are soluble in cyclopentane liquid phase. Cyclopentane hydrate crystals grew at the interface of cyclopentane and water to form a polycrystalline layer. We visually analyzed the individual crystals and classified the morphology of the hydrate crystals according to the subcooling ($\Delta.T_{sub}$) from the cyclopentane hydrate equilibrium temperature of atmospheric pressure. It was found that the size of the individual cyclopentane hydrate crystals decreased with increasing ΔT_{sub}. The results showed that the morphology of the individual cyclopentane hydrate crystals in any surfactant system is qualitatively similar at a given ΔT_{sub}. The observations also showed the three patterns of the behavior of the cyclopentane hydrate crystal growth depending on ΔT_{sub}, the chemical species of the surfactants and their concentration. (**i**) Crystal growth was similar to that in pure cyclopentane system without surfactant; (**ii**) Surfactants worked as inhibitors and prevented the crystal growth; and (**iii**) After the crystals grew at the interface, the hydrate crystals detached from the interface and fell into the water phase. These observations indicate that the surfactants have the effect of inhibitor and change the wettability of hydrate, cyclopentane and water.

Keywords: clathrate; hydrates; Crystal enginnering; Crystal growth; Energy transfer;

Green Chemistry – III

O-301

NOVEL CATALYSTS FROM WASTE BIOMASS: SYNTHESIS, PROPERTIES AND APPLICATION TO THE OBTAINMENT OF BIODIESEL FROM ALGAE

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Some important sources of oil, as waste cooking oils and oils from cultured microalgae, cannot be used for synthesizing biodiesel by alkaline catalysis because of their high free fatty acids content. Acids catalysts, homogeneous (e.g. H_2SO_4) or heterogeneous (e.g. ion-exchange resins) could represent an alternative, but they suffer of some important drawbacks. Ion exchange resins are expensive and do not resist to mechanical stress; H_2SO_4 is highly corrosive and require neutralization extra step.

Solid acid catalysts, prepared from cheap and easily available renewable sources represent a more sustainable alternative. In the present study, new solid acid catalysts have been prepared from sulfonation of carbonaceous material resulting from the pyrolysis of sugar beet molasses, the cheap viscous by-product of the production of sugar, and waste products, like potato peels. Pyrolysis conditions for molasses and potatoes peel carbons preparation (temperature and time) was very important in determining the performances of the catalysts; the best combination came from pyrolysis at low temperature (420 °C) for relatively long time (between 8 and 15 h), which ensured a better stability to the final material. The catalyst resulted to be highly active in the methanol esterification of fatty acids (100% yield after 3 h) as well as in the transesterification of acidic vegetable oils (55–96% yield after 8 h). Finally a “tandem process” using solid acid molasses catalyst followed by potassium hydroxide in methanol was developed to effectively convert algal oils containing high amounts of free fatty acids into biodiesel.[1]

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Keywords: *Solid acid catalyst; esterification; biodiesel; pyrolytic carbon; sulfonation;*

Green Chemistry – III

O-302

INVESTIGATION OF CATALYTIC AND PHOTOCATALYTIC PROPERTIES OF ZNO NANOFLOWERS WITH NOVEL FACETING

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A novel flower-like and holes-rich ZnO nanostructured catalyst, possessing 6-fold building blocks and wurtzite structure with [011^{-}0] orientation that shows activity for the hydrogenation of CO_2 is investigated. The evidence for this activity was shown with a Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) study. From the DRIFTS analysis it is known that methanol is formed at atmospheric pressure and relatively low temperatures with this novel ZnO catalyst. The photocatalytic decomposition of methylene blue was also studied using nanostructured ZnO that was modified with Li, Au and Ag. Results show that Li is detrimental to the photocatalytic activity, while Au and Ag increase the activity due to the electron transfer between ZnO and novel nanoparticles.

Keywords: *Nanostructures; Heterogeneous catalysis; Photocatalysis; Green Chemistry;*

Green Chemistry – III

O-303

SUSTAINABLE CHEMISTRY IN PRACTICE

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The world is facing unprecedented challenges, which are powerful drivers for change in society and economy. The developments in Sustainable chemistry (SC) are essential to master these through innovation, while balancing the 3 aspects of Sustainable Development (SD) (ecologic, economic and societal dimension). For society these can offer major global market opportunities for jobs and growth, if research on SC can be successfully transferred into broadly available innovative products and processes. In order to be successful academia and industrial players from the chemical sector and along the value chain have to work together.

Parameters to measure the progress on SC have to include molecular work (like on “Green Chemistry”) as well as the specific uses along the value chain till disposal. Validated approaches are urgently needed including acceptable screening criteria as neither raising unwarranted expectations in policy and the public nor “green washing” by any stakeholder is acceptable anymore. Life cycle assessment approaches can be useful as a measuring tool and guiding principle. However it must be recognized that these complex tools are not easily suited for communication to the general public and dependent on regional parameters. At global level it is essential to optimize a variety of parameters in the direction of SD due to the different framework conditions. Improved education on sustainability as part of students and employees curricula is vital. Interested stakeholders have to find new ways of cooperation like around the EU Technology and Innovation Platform for Sustainable Chemistry (SusChem).

The European Chemical Industry has established a coherent open and cooperative program to tackle these challenges, which will be presented and discussed.

Green Chemistry – IV

O-432

SYNTHESIS OF CYCLIC CARBONATES FROM WASTE CARBON DIOXIDE

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World-wide production of oil and gas is expected to peak before 2020. Therefore, since over 90% of all commercially available organic chemicals are sourced from crude oil, a major challenge for chemistry over the next 10 years is to find alternative, sustainable feedstocks for the chemicals industry. One particularly attractive reaction in this respect is the 100% atom economical reaction between CO_2 and epoxides leading to cyclic carbonates. Cyclic carbonates are already manufactured commercially and have a number of applications including as electrolytes for lithium ion batteries and as polar aprotic solvents.

In this presentation, the development of bimetallic aluminium(salen) based catalysts which, in the presence of a tetraalkylammonium cocatalyst, allow this reaction to be achieved at atmospheric pressure and room temperature will be discussed. Mechanistic studies on cyclic carbonate synthesis using these catalysts will be presented, which subsequently led to the synthesis of one–component versions of the catalysts. The immobilisation of the one–component catalysts on inorganic supports and their use in gas–phase flow reactors at temperatures and pressures suitable for direct utilization of power station flue–gas will be described. The tolerance of the catalysts to the NO_x and SO_x impurities present in simulated flue–gas will be reported as will the results of studies in which the catalysts were exposed to real flue gas from a combustion test–rig burning natural gas or coal.

In view of the scale of the possible use of the catalysts (up to 50 tonnes of catalyst per reactor), it is essential that the cost of catalyst production is as low as possible. Therefore, a cost analysis of the catalysts will be presented along with a modified synthesis which avoids all of the expensive reagents and solvents.

Keywords: *carbon dioxide fixation; aluminium; sustainable chemistry;*

Green Chemistry – IV

O-433

DIMETHYL CARBONATE AS GREEN REAGENT FOR CHLORINE-FREE SYNTHESIS

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Dialkyl carbonate (DACs) in general, and dimethyl carbonate (DMC) in particular, are well recognized green reagents and solvents for new synthetic pathways. DMC, nowadays synthesized by CO_2 insertion into epoxides, has shown surprising high selectivity with different monodentate and bidentate nucleophiles. DMC can act as methoxycarbonylation agent via a $B_{Ac}2$ mechanism at reflux temperature and as methylating agent via a $B_{Al}2$ mechanism at higher temperature. Both reactions give as only by-product methanol and eventually CO_2.

In this work, we report recent advances in DMC chemistry for chlorine-free synthesis of 5- and 6-membered heterocycles and for the synthesis of nitrogen and sulphur half-mustards carbonate analogues.

In particular, the reaction of 1,4-diols with DMC in the presence of a base resulted in the chlorine-free synthesis of 5-membered cyclic compounds. This reaction pathway to cyclic ethers is of general application as it can be employed for the preparation of small heterocycles as well as of industrially relevant compounds *i.e.* (-)-norlabdane oxide and isosorbide. This synthetic procedure can be also used for the quantitative *intramolecular* heterocyclisation of bifunctional compounds *i.e.* 4-amino-1-butanol to achieve pyrrolidine.

Six-member cyclic carbamates have also been synthesised by chlorine-free approach employing DMC chemistry. In fact, reacting a primary amine or a hydrazine with a di(methyl carbonate) derivative of 1,3-diols oxazinan-2-ones can be synthetised in a one-pot chlorine-free reaction.

Recently we also investigated the replacement of the chlorine by a carbonate moiety in half-nitrogen and -sulphur mustard compounds. This resulted in new, unexplored and safe compounds that showed good reactivity. Results collected demonstrated that the novel mustard carbonates are easily synthetised, don't show any toxicity and react with a wide range of nucleophiles in the absence of any base.

Keywords: *Dimethyl Carbonate; Cyclisation; Heterocycles; Mustard Compounds; Green Chemistry;*

Green Chemistry – IV

O-434

TRACES OF DEGRADATION BY PYROLYSIS UNDER ULTRASOUND: IT'S GETTING HOT IN IONIC LIQUIDS!

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More than eight decades after the discovery of ultrasound-induced chemical processes, known as sonochemistry, they remain a subject of attractive research. It is generally accepted that the chemical effects of ultrasound result from the phenomenon of acoustic cavitation, which is the formation, growth and collapse of bubbles in an elastic liquid. By imploding, these bubbles create locally extreme conditions that can lead to high-energy radical mechanisms but also generate some interesting physical effects that can improve catalyst activity.

Since the use of ionic liquids in organic chemistry as solvents and/or as catalysts and since the development of organic sonochemistry, the combination of these two technologies has presented unsuspected and very beneficial effects for certain organic reactions. However, the effects of ultrasound on ionic liquids are unknown, except the observation of a darkening of the ionic liquid of the study by several research groups.

For the first time, we have determined the origin of this coloration through the behaviour of hydrophobic ionic liquids to the phenomenon of cavitation. We have studied the sonoluminescence of pyrrolidinium and piperidinium ionic liquids. We have identified, from recent and advanced analytical methods, the main traces of degradation products in order to propose mechanisms of degradation of ionic liquids under ultrasound. Moreover, we have developed a simple and convenient method to significantly reduce the impact of ultrasound on ionic liquids and thus protect them from degradation. For the first time, we determine the acoustic power when they are submitted to ultrasound. Ionic liquids heat up almost three times faster than water leading to interesting effects as solvent for organic reactions.

Our original studies present a real important impact for researchers for a better understanding of ionic liquids/ultrasound combination for various organic chemistry applications, and not only for specialized scope.

Keywords: *ionic liquids; analytical methods; green chemistry;*

Green Chemistry – IV

O-435

PHASE EQUILIBRIA OF CLATHRATE HYDRATES SUITABLE FOR CARBON DIOXIDE CAPTURE

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This study is concerned with the technology for CO_2 separation from gas mixture utilizing clathrate hydrate formation/dissociation. CO_2 separation may be applied for flue gas from combustion power plants (CO_2 and N_2 mixture) or for unconventional natural gas such as coal bed methane and biogas (CO_2 and CH_4 mixture). The obstacle of this hydrate technology is high pressure for hydrate formations. Hence, it is favorable to moderate equilibrium conditions by adding hydrate formation promoters such as ionic guest substances which form semiclathrate hydrates. In the present study, ionic guest substances were selected based on the following three requirements: (**a**) moderate the equilibrium conditions, (**b**) non-toxic, non-flammable and non-corrossive effect on metal and (**c**) store large amounts of gas. Among the selected candidate guests, we particularly focused on tetrabutylphosphonium bromide (TBPB) hydrate and tetrabutylphosphonium chloride (TBPC) hydrate. This paper reports an experimental study on the phase equilibrium measurements in three-component systems of (CO_2, CH_4 or N_2 + TBPB + water) and (CO_2 or CH_4 + TBPC + water). These experimental data were measured by isochoric method in the pressure (p) range of (0.1 to 2.1 MPa) and temperature (T) range of (282 to 289 K) at mass fraction 0.35 for TBPB and 0.36 for TBPC. The measurement uncertainties were ±0.1 K for T, ±5.0 kPa for p, and $\pm 1.0\times10^{-4}$ for mass fraction of each species in the liquid phase. It was found that equilibrium conditions for the (CO_2 or CH_4 + water) systems were more moderated by TBPB than by TBPC. The results also indicated that TBPB was better ionic guest substance for CO_2 separation from CO_2 and CH_4 mixture than TBPC.

Keywords: *Clathrates; Hydrates; Carbon dioxide fixation; Green chemistry; Phase diagrams;*

Green Chemistry – V

O-436

NEW SYNTHETIC TOOLS FOR THE DEFINITION OF SUSTAINABLE CONTINUOUS-FLOW REACTORS

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Our research program is committed to the definition of waste-minimized and eco-friendly synthetic procedures for the production of fine chemicals using water[1] or solvent-free conditions (SolFC).[2]

Our goal is to take green chemistry principles in flow by defining novel sustainable processes based on the combination of heterogeneous catalysts and continuous-flow reactors able to operate in safer media and to drastically reduce waste production.

This approach should allow **a**) the highest intimacy between the reactants and their optimal access to the catalytic sites, **b**) to avoid mechanical stirring and high pressures and **c**) the recovery of the final products using the minimal amount of organic solvents and therefore minimizing the production of waste.

Commercially available solid supports (organic or inorganic) have been developed to be used in the presence of a reaction medium and designed to deal with the related swelling processes. Besides, mechanical stirring of the reaction mixture often causes the complete crunching of the solid catalyst hampering its recovery and reuse.

Our current studies are mainly directed towards the design and synthesis of tailor-made supports able to be effectively used in continuous-flow reactors operating under SolFC or in the presence of a dispersion medium such as water. The novel solid supports should mainly solve the problems related to their swelling and the consequent internal pressure.

Some examples from our laboratory will be presented in this communication.

Acknowledgement: *This research has been supported by MIUR within the programs: PRIN 2008, FIRB – Futuro in Ricerca 2008*

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   b) *Green Chem.* 2012, *14*, 164;
   c) *Adv. Synth. Cat.* 2010, *352*, 2489;
   d) *Green Chem.* 2010, *12*, 1301

Keywords: *clean synthesis; flow chemistry; heterogenous catalysis; water; solvent-free conditions;*

Green Chemistry – V

O-437

SUCCESSFUL APPLICATION OF POROUS GLASSES AS SUPPORT FOR METHANE EMISSION REDUCTION CATALYSTS

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The use of methane as fuel for natural gas vehicles is increasing, although a still unsolved problem is the remaining methane content of 500 to 5000 ppm in the exhaust gas stream.[1] For the abatement of these emissions low temperature methane oxidation can be used, which has been extensively studied[2, 3] but not yet applied for this purpose. Apart from complete conversion at low temperatures the long term stability is the major requirement that can often not be fulfilled.[4]

This work presents the application of porous glasses as support for Pd/CeO_2 catalysts providing a protective framework, reducing the methane activation temperature and increasing the long term stability.

Catalysts composed of Pd on CeO_2 in porous glasses were prepared by simultaneous or consecutive impregnation. The influence of impregnation procedure, glass pore size and palladium loading on the catalytic activity for CH_4 oxidation was investigated and interpreted by H_2-TPR. Consecutive impregnation of the glass support with cerium nitrate melt and palladium nitrate solution yielded outstanding results in combination with a glass pore size of 151 nm. Methane conversion reached 100% at temperatures as low as 350 °C in case of a 1% Pd loading related to CeO_2 and 305 °C with 10% Pd loading respectively. Long term stability tests were carried out showing the steadiness of the catalysts during 50 hours on stream. No pre-treatment of the catalysts was necessary, granting a fast start-up.

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Keywords: *Heterogeneous catalysis; Oxidation; Palladium; Cerium; Glasses;*

Green Chemistry – V

O-438

HETEROGENEOUS CATALYTIC OXIDATION AND CARBONYLATION REACTIONS IN A GAS/LIQUID CONTINUOUS FLOW REACTOR

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Gas/liquid phase heterogeneous catalytic reactions with simple added gas components (hydrogen, oxygen, carbon monoxide, etc.) are very efficient and green processes in the pharmaceutical, agro and fine chemical industry as well as in R&D. Employing traceless gaseous reagents over chemicals allows to develop greener processes reducing the waste and the purification burden. While hydrogenation is extensively used in continuous flow processes due to the availability of safe *in situ* generation of this gas in a flow reactor oxidation with molecular oxygen or (hydro)formylation with CO are not fully exploited due to the strict technological requirements for safe operation. In a recent edition of a fixed-bed continuous flow reactor various external gas components can be applied including O_2, CO or CO_2. In the presentation various oxidation reactions with elementary oxygen (including aromatization, convertion of primary and secondary alcohols to aldehydes vs. ketones, Baeyer-Villiger oxidation etc.) as well as carbonylation and carboxylation will demonstrate the various novel opportunities in continuous flow. The reactor cartridge could be pre-packed with various types of catalysts including Au/TiO_2, Ru/C, Ru/Al_2O_3, Pd/C etc, which avoids leakage (external purification) and allows the reuse of the catalyst.

Keywords: *continuous flow chemistry; microreactors; heterogeneous catalytic oxdation;*

Green Chemistry – VI

O-439

NOVEL METHODOLOGIES FOR ABATEMENT, CONCENTRATION AND UTILIZATION OF FLUE GAS POLLUTANTS BASED ON IONIC LIQUIDS

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Burning of fossil fuels for power generation is always accompanied with formation of awfully undesired pollutants which are environmentally damaging and typically highly toxic. Even renewable fuels such as biodiesel, bioethanol and even hydrogen are expected to generate toxic contaminants particularly oxides of nitrogen. Although some upstream purification methods are exercised e.g. hydrodesulfurization at the oil refinery, the large majority of cleansing techniques are end of pipe solutions. While the traditional abatement methods focused on neutralization and decontamination of the pollutants, novel technologies are seeking approaches to convert the pollutants into useful products e.g. sulfate or nitrite fertilizers, sulfuric or nitric acid and purified heavy metals.

We have recently found that ionic liquids (ILs) are superb conduit for the abatement of flue gas pollutants using standard gas liquid scrubbers. Typical ILs such as BMIM (1-butyl-3--methylimidazolium) halides form stable adducts with sulfur dioxide that allow the swift and quantitative removal of SO_2 from the gas phase. After absorption the BMIM-SO_2 complex can be straightforwardly decomposed by a temperature swing or by using a recycleable polar solvent, such as alcohol, that readily releases pure SO_2. The latter can be directly used as raw material for various commercial products.

It was further realized that the absorption characteristics of imidazolium based ILs can be considerably upgraded by incorporation of oxidizing agents. Mercury was shown to be swiftly oxidized and captured from flue gas of burning coal under very mild conditions, using iodine adducts of BMIM halides. Another interesting hybrid reagent, developed in our laboratory is the complex of ClO_2 with BMIM halide. This novel adduct was demonstrated to function as a three way absorption reagent in a common gas/liquid scrubber. The reagent simultaneously captures mercury, SOx and NO_x by an oxidation process converting the latter into aqueous sulfate and nitrates that can be used as fertilizers. The mercury, trapped as a complex $BMIM^+ HgX_3^-$, can be recovered in a pure form e.g. by reduction with aqueous sodium formate. This example exhibits an incredible concentration factor (10^9) achieved via a remarkably simple and cost effective operation.

Further details will be presented at the lecture.

Keywords: *Mercury; Sulfur oxides; Nitrogen oxides; Flue gas purification;*

Green Chemistry – VI

O-440

NON AQUEOUS SOLVENT FORMULATIONS BASED ON 2-AMINO-2-METHYL-1-PROPANOL (AMP) FOR EFFICIENT CO_2 ABSORPTION AND LOW TEMPERATURE DESORPTION

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Although the CO_2 capture using aqueous alkanolamines is considered the most efficient and feasible technique, the energy required for the solvent regeneration and the alkanolamine degradation are the bottleneck of the process still requiring unacceptable energy and economic costs.[3] We have formulated non aqueous solvents with the objective of minimizing the drawbacks of the aqueous alkanolamines without reducing their advantages. The solvents are based on AMP-alkanolamine blends (alkanolamine: 2,2'-iminodiethanol, DEA; N-methyl-2,2'-iminodiethanol, MDEA; N-methyl-2-aminoethanol, MMEA; bis(2-hydroxypropyl)amine, DIPA; overall, 2.0 M; 18.3-22.6 wt %) and either single alcohols or mixtures with ethylene glycol. Throughout the experiments of CO_2 capture (12 % v/v in air), both carbonated and regenerated solvents are continuously circulated in a closed system between the absorber (20 °C) and the desorber (65, 70, 75, 80 °C). The CO_2 loading capacity and the absorption efficiency at equilibrium are in the range 0.65–0.81 (on molar scale, with respect to the amine) and, respectively, 73.1–95.9 %, depending on the composition of the solvents and the desorption temperature. The carbon containing species in the CO_2-amine-alcohol equilibria have been analysed by ^{13}C NMR spectroscopy[2] and have been found to originate from alcohol and amine carboxylation. The lower stripping temperatures should reduce the thermal and oxidative degradation of the amines, whereas the lower heat capacity of alcohols combined with the lower stripping temperatures could offer potential advantages in terms of energy saving with respect to conventional aqueous alkanolamines. In some experiments, AMP carbamate has been obtained in the solid state and its peculiar reactivity towards some alcohols has been tested.

***Acknowledgements:** This work was financially supported by ENEA (Rome).*

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Keywords: *carbon dioxide fixation; carboxylation;*

Green Chemistry – VI

O-441

DEVELOPMENT AND APPLICATION OF NOVEL BIOINSPIRED IONIC LIQUIDS

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Biological molecules are considered as building blocks of life. The understanding and use of their chemistry represents a crucial role in modern research science.[1] In last decades, Ionic Liquids (ILs) have emerged as a possible environmentally benign alternative to common organic solvents, due to use in a variety of areas.[2] In this context, Novel Functional Bioinspired ILs (FBILs) based on the incorporation of relevant biological molecules by simple dissolution (e.g. ILs and cyclodextrins) or by sustainable synthetic combinations (e.g. chiral ILs based on aminoacids such as L-cysteine derivatives) have been developed.

The main goal is related with the development of novel Chiral biomaterials based on the interaction of biocompatible ILs and cyclodextrins as well as the preparation of L-cysteine derivatives as chiral ILs. Applications of this novel Chiral ILs include their use for chiral recognition processes and chiral media for asymmetric catalysis.[3]

Two different approaches have been investigated: (**i**) dissolution and interaction studies of α, β and γ cyclodextrins (CDs) with several ILs. Their dissolution performance and interaction behavior have been studied. Novel biomaterials based on simple combination of ILs and CDs can be applied for host-guest and drug delivery processes[4]; (**ii**) preparation and characterization of novel chiral ILs based on L-cysteine derivatives such as S-methyl-L-cysteine and S-carboxymethyl-L-cysteine combined with appropriate counter-ions. The most promising chiral ILs has been applied for enantiomeric resolution and asymmetric catalytic reactions.

Novel biocompatible materials based on the combination of ILs and CDs can be explored for relevant chiral discrimination or separation processes. Novel L-cysteine ILs have been tested for resolution of racemates as well as chiral media for asymmetric aldol and Michael reactions.[5] Their efficiency should be dependent of the combination of L-cysteine as cation or anion with appropriate counter-ions.

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Keywords: *Amino acids; Ionic liquids; Green chemistry; Asymmetric catalysis; Chirality;*

Green Chemistry – VI

O-442

REDOX-ACTIVE VANADIUM POLYOXOMETALATES FOR ENERGY PRODUCTION AND STORAGE

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Polyoxometalates (POMs) are anionic molecular oxides of early transition metals, such as Mo, W, V and Nb, which possess an unmatched ability to incorporate almost every single element from the periodic table in their structure. This rich elemental composition together with a vast diversity in size and topology help to explain their extraordinary flexibility in a range of physical properties. For instance, POMs are generally soluble in water yet they can be made soluble in a range of organic solvents and they tend to exhibit a wealth of redox processes whilst keeping their structure intact. These, in particular, make POMs ideal candidates for energy storage and catalytic applications related to green energy production.

In this light, we present $[P_4V_6W_{30}O_{120}]^{10-}$, a Wells–Dawson polyoxometalate sandwich compound with a double cubane core consisting of six vanadium atoms[1]. The formation of the cluster is followed by mass spectrometry and the reduction of the double cubane is studied by a novel technique combining mass spectrometry and spectroelectrochemistry. Catalytic properties of $[P_4V_6W_{30}O_{120}]^{10-}$ are evaluated in connection with solar fuels production and compared to other members of the vanadium polyoxotungstate family. A new device concept is also presented linking the ideas of energy production and storage in one molecular system.

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Keywords: *Polyoxometalates; Vanadium; Mass spectrometry; Electrochemistry;*

Green Chemistry – VI

O-443

EXPERIMENTAL AND THEORETICAL COMPARISON OF AN EQUATION OF STATE FOR PORE-CONFINED FLUIDS

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The prediction of properties in porous materials is of continuing interest in the fields of chemical and materials engineering. Application areas include, among others: (**a**) the use of supercritical fluids to modify porous materials, (**b**) physical adsorption of trace components from gaseous effluents, (**c**) gas storage using micro-porous materials, and (**d**) chemical separations using inorganic membranes.

There is a need for useful thermodynamic models in this area and here we present an equation of state (EOS) for calculating the thermodynamic properties of both bulk and pore-confined fluids. We illustrate for the first time the application of this EOS to both realistic bulk and single component adsorption systems. The model is a mean field type derived from a statistical mechanics approach carried out in the grand canonical ensemble. In pure fluids, the only properties required are the bulk fluid's critical properties. In adsorption systems, the fluid-solid matrix interaction parameter is required.

We show comparisons between the model and the Peng-Robinson (PR) equation of state, for methane and carbon dioxide in the bulk fluid case. However, our EOS has an important advantage over the original PR EOS in that it seamlessly carries over into predictions of the pore-confined fluid thermodynamic properties. We illustrate this point using recently published adsorption data in a carbon dioxide-silica aerogel system.

Keywords: *Supercritical fluids; Adsorption; Statistical thermodynamics;*

EYCN – The art of writing

O-166

THE ART OF WRITING: FROM TELL TO SELL

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Writing a scientific paper is something that many scientists enjoy and others dread. The value of writing a paper in a concise, engaging and clear way, normally translates to a higher impact of your scientific work. Top articles are normally well-written, read, remembered and highly cited, whilst poorly written papers are easily forgotten.

However, good writing is not simple and depends on many different factors as the journal, type of manuscript, concepts to report and readers, for example. So that, there is not a single, correct way to write, because many different solutions to the problem are possible.

In this communication, an overview of the elements of style and composition of a scientific paper will be discussed. In addition, different approaches for an effective and successful writing outcome will be reviewed and adapted to young chemists that are in the early stage of their career.

Keywords: *Inorganic Chemistry; Organic Chemistry; Physical Chemistry; Writing;*

EYCN – The art of writing

O-167

WRITING PROPOSALS EFFICIENTLY AND EFFECTIVELY

S. GOMEZ-RUIZ [1]

[1] *Universidad Rey Juan Carlos, Department of Inorganic and Analytical Chemistry, Mostoles (Madrid), Spain*

This workshop will be focused on the art of writing a grant proposal. Usually, the process of planning and of presenting your research ideas or results to the right person takes time and persistence to succeed.

Techniques and advices for an efficient way of writing will be discussed in this lecture. It will emphasize topics such as idea development and identification of the most appropriate funding sources and the basic components of a proposal.

Participants will learn the common mistakes and reasons why sometimes well written proposals finally fail. Budget preparation and review criteria and tips for writing succeessful proposals will be also examined.

The final part will be for discussion of questions and doubts from the Audience.

Keywords: *writing; grant proposals; chemistry proposals;*

EYCN – Putting your degree to work

O-168

PUTTING YOUR DEGREE TO WORK

S. HOBBS[1]

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What does a set of keys and a Chemistry degree have in common? They both open many doors. Wondering what you can do with your Chemistry degree? Come along to the RSC's careers talk to find out more. The talk will cover career profiles from a selection of chemists, demonstrating the wide variety of options open to those with a chemistry background. The careers focus will be looking at the path from a PhD to a non-academic profession and learning to cope with the change in environment. Additionally we will be looking at an example of a graduate scheme from application to assessment day and interview.

Finally, there will be additional information highlighting the resources available from the RSC Careers Service. The RSC's careers service offers its members the support they need to enhance their skills or develop new ones, help with a change of direction in their career, advice with job hunting including advice on the recruitment process, including CVs, application forms and interviews. The importance of effective individual career planning can't be overestimated in today's volatile job market, so whether you are just starting out on your career path or well on your way through it, the RSC has resources to help its members.

Please bring a copy of your CV to this session, they will not be checked individually but will form part of an exercise.

EYCN – Chemethics and eCV

O-169

ETHICS IN SCIENCE AND TECHNOLOGY

A. QUINTANILHA[1]

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As human beings our way of dealing with curiosity and imagination has evolved significantly over the centuries. Whatever the field of knowledge, whether astronomy, chemistry, biology, sociology or philosophy, it was always because we were disatisfied with existing ideas, that new questions and tentative new answers took shape, which required novel ways of validation. At the interface of science and philosopy new forms of ethics, namely bio-ethics, gen-ethics or eco-ethics have flourished over the last decades. We will discuss current issues in these emerging domains of knowledge. Risk, equity and fraud will be used as examples to illustrate the presentation.

EYCN – Chemethics and eCV

O-170

YOUR E-CV: OPTIMIZING SOCIAL MEDIA

M. AGOSTINHO[1]

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Finding a job is getting more and more difficult under the current economy. Nowadays, social media plays a big role in employee hiring, and therefore it is important to think outside the box. It is also crucial to make use of such tools in promoting soft and hard skills to achieve maximum impact in companies and academia. Tools such as ResearchGate, LinkedIn, Twitter and Facebook, are a privileged platform of professional promotion and networking. For instance, LinkedIn, a vast professional social network, enables users to demonstrate what they can convey to prospect employers. With the current challenges that Science poses to young researchers, it is essential to develop and promote a set of skills that leads to a higher rate of employability. With this lecture we intend to give some highlights on how to use social media in the search for a new job or simply to endorse the work researchers carry out and to establish a solid scientific career.

As part of a CV, young researchers are encouraged to demonstrate their personal attributes that enhance not only interactions with fellows in the field, but also job performance and career prospects. Through the use of these digital platforms, it is possible to show positive attitude, self-confidence, communicational skills and team spirit, essential characteristics to succeed in any work field.

EYCN – Making chemistry work for you

O-304

EYCN MAKES CHEMISTRY WORK FOR YOU

V. FLUXA[1]

[1] *EYCN, EYCN board, Berne, Switzerland*

The European Young Chemists' Network (**EYCN**) is an organisation representing the young members of the European Association for Chemical and Molecular Sciences (EuCheMS). Every chemist under 35 within the EuCheMS framework is part of EYCN. For the last 6 years we have worked towards promoting the exchange of knowledge among chemists in academia and industry, as well as professional institutions and government bodies across Europe.

In a friendly environment, we aim to bridge the gap between your studies and your chemical career. Are you thinking of going to the U.S. for a Postdoc or PhD? During this session, a delegation of American students will be there for you. To answer and discuss your doubts and help you plan your decision of going abroad.

Initially launched with 12 participating societies, EYCN today encompasses the knowledge and enthusiasm of young chemists from 24 chemical societies in Europe and abroad. Our energy goes to support and encourage young chemists at the beginning of their careers. Following from that idea we have organised activities designed to develop the tools for undergraduate and graduate students to improve their career possibilities. Workshops in interview skills and CV writing and seminars about development of soft skills are our main events during the EYCN Satellite Event during the Prague Congress.

You can follow us on Facebook, Twitter, LinkedIn, and on our web page www.eycn.eu. Join our informal session, get to know the network and become part of a giant multicultural voice.

Keywords: *eycn; career days; young chemist; network;*

EYCN – Making chemistry work for you

O-305

BEER: FROM THE FIRST GLASS TO A HANGOVER

K. ROTH[1]

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Beer brewed according to the German "*Reinheitsgebot*" or purity law is regarded as the quintessence of an unadulterated food produced without any "chemistry". What an error! There is so much exciting chemistry involved all the way from barley to a glass of beer in front of us. The chemical climax is the conversion of some hop constituents into bittering substances via a breathtaking a-ketol- or *Oktoberfest*-rearrangement. This is just another proof that chemistry cannot only be exciting but can also taste good. But there is a dark side. After too much beer drinking there arises what is colloquially referred as a "hangover" with all its terrible symptoms. How can a tiny molecule like ethanol be at the root of so much human misery. Let's get to the bottom of the chemical consequences of a night of celebrating to excess. Well then: *Na Zdraví!*

Keywords: *alcohols; medical chemistry; metabolism; rearrangement;*

Sustainable food production – I

O-031

CHEMISTRY FOR SUSTAINABLE FOOD PRODUCTION

B. WEDZICHA[1]

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The word 'sustainable' means different things to different people, and it is difficult to reach a consensus with regard to its significance with regard to food production. On the one hand, the energy equation and environmental aspects (e.g., water, emissions, distribution) feature strongly in the sustainability argument, whereas the scope of sustainable food production must include manufacture efficiency, the utilisation of by-products (e.g., chemical, mechanical, heat), and reduction in waste up to the point of consumption. However, unless the food is good to eat and consumers are offered adequate choice (in both quality and type of food) the industry fails to main itself in a financially sustainable condition. Thus food quality (texture, flavour, safety) and shelf-life considerations are an important aspect of the sustainable food industry. This talk will explain these considerations and show how they will be addressed through the contributions to the conference.

Keywords: *KInetics;*

Sustainable food production – I

O-032

FOOD PRODUCTION AND FOOD QUALITY: A SUSTAINABLE MATCH

M. VAN BOEKEL[1]

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The production of food is obviously of high importance from a societal point of view, but at the same time it can be stated that food production systems are not (yet) optimized in terms of sustainability. The focus so far has been much more on being effective than on being efficient, in terms of the use of available resources. Scarcity of resources (energy sources, raw materials, clean water) in the very near future will be a challenge to produce food in enough amounts for a growing world population. In the past 100 years or so, much has been achieved in terms of food security, food safety and food quality. The challenge to keep these high standards while the resources are becoming scarcer is enormous. It becomes all the more necessary to involve a scientific and engineering approach to tackle this challenge. To calculate the impact of using scarce resources and producing waste and side-streams that are given back to the environment, a thermodynamic approach is proposed by modelling food production activities in terms of entropy production. At the same time, food quality should be maintained and optimized, and this requires another modelling approach in order to get a grip on the multidimensional aspects involved. Thus, understanding, controlling, and prediction of food quality and safety by using mathematical models is proposed as a way forward to make food production more sustainable while still delivering high quality foods. This lecture will address some of the basic principles that are needed to come to such an approach.

Keywords: *food quality; food production; sustainability; food safety; thermodynamics;*

Analytical chemistry supports sustainable food production

O-033

ANALYTICAL CHEMISTRY SUPPORTS SUSTAINABLE FOOD PRODUCTION

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[1] *Institute of Food Chemistry, University of Hamburg, Hamburg, Germany*

Food analysis must be considered in regard to the type of matrix, the amount of information required, the legislation, and the possibilities of the laboratory. Developments in the creation of new analytical tools can help to improve the quality of food as well as to assist sustainable production of food. The aims of sustainable production of food are to protect the natural sources and to produce food with high quality. Food quality cannot only be described by single parameters such as contaminant content and major nutritional constituents. It comprises the consumer expectations like nutritional, sensory, technological value as well as food safety aspects. The analytical process of food comprises sampling, extraction, sample preparation and analysis, it is a complex system. Analytical methods can be divided into fast methods used during food. production, sensitive methods for known compounds used during food surveillance and most sensitive and versatile methods for unknown compounds and metabolites used in research institutes.

In the lecture are given examples how to solve recent analytical problems which are connected with food safety and food production. These examples comprise food allergenicity, contaminations and residues, GMO identification and identification of trans fatty acids (TFA).

Microconstituents and analysis

O-034

THE ROLE OF THE FLAVOUR CHEMIST IN MAINTAINING SUSTAINABLE FOOD PRODUCTION

J. PARKER[1]

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With the UN predicting that world food production must rise by 50% by 2030 to meet increasing demand, and additional threats from climate change, agronomists are selectively breeding high yielding, drought resistant crop varieties for the future. Process engineers are tasked with reducing energy and water requirements, for which a parallel increase in demand is forecast. How can we, as chemists, and particularly flavour chemists, contribute to sustainable food production?

Whilst yield and nitrogen efficiency are key indicators of success, it is recognised that the consumer still expects a high quality product and is unwilling to sacrifice the flavour when selecting a product which is more healthy, ethical or sustainable. It is, therefore, of utmost importance that flavour quality is considered when manipulating varieties or processing conditions in search of a more sustainable product. This is where it becomes crucial to understand the chemistry involved in flavour generation.

Flavour can either be generated in situ from endogenous precursors, or it can be added as part of a flavouring preparation. Flavour houses are already addressing the sustainability issue. Biochemists are involved in “white biotechnology” generating flavour compounds (or their precursors) from renewable resources using fermentations and biocatalysis. Synthetic chemists are designing novel pathways from renewable starting materials and developing highly selective, and ever increasingly efficient, catalysts.

As flavour chemists, our role is to maximise flavour production from raw materials where selective breeding has bred out flavour precursors, or minimal processing conditions have diminished flavour forming pathways. The major route to flavour generation during thermal processing is the Maillard reaction, a complex cascade of interdependent reactions. The flavour chemist of the future needs to have a thorough understanding of the mechanism involved and the critical control parameters, in order to maximise flavour formation in unfavourable, though sustainable, conditions.

Keywords: *sustainable food production; flavour formation; Maillard reaction;*

Monday, 27-Aug 2012

Microconstituents and analysis

O-035

CHARACTERIZATION OF CYPRIOT HONEYS BY USING NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

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[4] *Food lab Ltd, Chemistry, Nicosia, Cyprus*
[5] *Univercity of Cyprus, Department of Chemistry, Nicosia, Cyprus*

Honey is an expensive natural food that has been, for a long time, target for adulteration and/or intentional misdescription of its botanical and geographical origin. Current, melissopalynilogical methods used for honey discrimination do not meet the quality standards of modern validated analytical methods. In this study, the geographical and botanical origin of Cypriot and Greek honey is investigated utilizing the NMR spectroscopy. Proton and carbon NMR are the well known techniques used for analytical purposes. NMR spectroscopy is a very useful tool for food analysis because (**a**) it is non catastrophic method for the sample, (**b**) it doesn't require a lot of quantity of the sample (**c**) it is fast, and (**d**) gives high resolution: in a single run it is able to give a rich of information for many components. Proton and carbon NMR spectra have been recorded for deuterium oxide solutions of honey samples and standards at room temperature. From spectral analysis, the sugars content, amino acids, and the glucose/fructose ratio of honeys have been determined. It has been found that the profile of sugars isoforms is strongly dependent on the flora diversity located at different altitudes of the island providing a good separation for Cypriot and Greek honeys. The prior classification of the honeys based on the altitude facilitated the geographical and regional discrimination of the honeys. Because honey is objected to adulteration through mixing with honey originated from non European countries these chemometrics promote the detection of adulteration of the Cypriot and Greek honeys. The determination of the glucose/fructose ratio alone consists an effective indicator for the origin of the samples, and in combination with the NMR spectroscopy provides a fast identification /quantification method for the product which highly concerns the food industry and the consumer's society.

Funding from Research Promotion Foundation and the European Structural Funds program: ΑΝΑΒΑΘΜΙSH/ΠΑΓΙΟ/0308/32

Keywords: *honey; NMR; chemometrics; adulteration; origin;*

Microconstituents and analysis

O-036

BOTANICAL DISCRIMINATION OF OLIVE OILS USING 19F NMR SPECTROSCOPY

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In the last decade there has been a rapidly increasing use of NMR spectroscopy in the field of Food Science, because of the advances in high field magnets and probe design that amplified the analytical capacities of modern NMR spectrometers. The most common applications are on food analysis, authentication and quality control of food stuff. The disadvantage of the lower sensitivity of NMR compared to other spectroscopic techniques such us UV-Vis, fluorescence, EPR etc. is compensated by its high resolution: a single scan provides a rich of information for many components in the assay. ^{1}H and ^{13}C nuclei are the target nuclei of the majority of the NMR experiments because of their high sensitivity, while other nuclei such ^{31}P have also been utilized. In this study, we develop a new method utilizing the ^{19}F NMR spectroscopy for exploitation to the olive oils analysis and apply for olive oil discrimination. The ^{19}F active adduct is chemically bound to the components containing -OH or –COOH groups. The fluorinated products exhibit hydrolytic and redox stability for long time and the ^{19}F NMR spectra were run in $CDCl_3$, giving chemical shifts ranged from -74 to -77 ppm, referenced to $CFCl_3$ (0 ppm). 30 samples of Olive oils from different botanical origin cultivated inCyprus have been examined with the above method. Utilizing 19F NMR spectroscopy several components such as α-tocopherol, tyrosol, mono- and diglycerides, β-sitosterol, desmesterol and free acids have been determined. PCA statistical analysis has been applied to the results and it has been found that there is a discrimination of the samples based on their botanical origin.

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Keywords: *Analytical Methods; NMR spectroscopy;*

Microconstituents and analysis

O-037

THE FREE RADICAL INVOLVED IN THE OXIDATION OF FLAVONOIDS BY LACCASE. AN ASSAY FOR PRO-OXIDANT REACTIVITY

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Under certain conditions polyphenolics may display prooxidant rather than antioxidant properties, and this may lead to undesirable consequences such as inhibition of mitochondrial respiration, direct DNA damage, lipid peroxidation and mutagenicity - but also to benefic effects such as tumor cell apoptosis, cytoprotective enzyme induction, or activation of oxidative-stress-responsive transcription factors.

Here, we describe a transient species that may be detected with UV-vis and EPR spectroscopy during turnover of a laccase with a polyphenolic compound – quercetin. This transient species is assigned as a quercetin-derived radical, based on EPR spectra as well as based on UV-vis similarities with previously reported data obtained via a non-enzymatic route. The formation and decay of this species correlate well with the prooxidant reactivity manifested by flavonoids in the presence of laccase. An assay for the prooxidant reactivity of natural compounds is proposed based on the results reported here and applied on several propolis extracts; this assay has the advantages of using a biologically-relevant process (hemoglobin oxidation), and of not needing added oxidizing agents such as peroxide or superoxide. A series of flavonoids are assayed with this method and their characteristics are discussed. Correlations, or the lack thereof, between the prooxidant parameters and the redox potentials, antioxidant capacities and lipophilicities are analyzed.

The advantage of using a laccase instead of a peroxidase is that it does not use H_2O_2 as co-substrate but O_2; indeed, H_2O_2 might have direct action on some compounds or it may generate reactive oxygen species due to traces of transition metals. Moreover, laccases are multicopper oxidases structurally and functionally similar to ceruloplasmin. This proposed assay for pro-oxidant activity would thus involve direct action of phenoxyl radicals of flavonoids, with no other reactive species needed.

Acknowledgement: *Financial support from POSDRU/88/1.5/S/60185 – "Innovative doctoral studies in a knowledge based society" is gratefully acknowledged by ACM.*

Keywords: *quercetin; flavonoid; radical; laccase; pro-oxidant;*

Microconstituents and analysis

O-038

ANTIRADICAL CAPACITY AND REDOX POTENTIAL OF PHENOLIC BETALAINS

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Betalains are natural pigments with high antioxidant capacity, which have been used as therapeutic agents in several conditions related to oxidative stress. In this work, we describe the semi-synthesis of artificial phenolic betalains and the pH dependence of antiradical capacity and redox potentials. Betalamic acid was obtained by alkaline hydrolysis of betanin and coupled with ortho-, meta- and para-aminophenol under acid conditions resulting in BtPh-2-OH, BtPh-3-OH and BtPh-4-OH (average yield = 50%). Products were purified by reversed-phase column chromatography and characterized by LC/ESI(+)-MS and NMR spectroscopy.

The antiradical capacity of the three regioisomers was evaluated using the TEAC/ABTS method and reported as Trolox equivalents. All betalains prepared have higher antiradical capacity than ascorbic acid and the vitamin E analogue Trolox. BtPh-3-OH has the highest TEAC (5.1 ± 0.3, pH = 7.4). The TEAC of BtPh-2-OH and BtPh-4-OH in the same experimental conditions was found to be 3.8 ± 0.3 and 3.0 ± 0.1, respectively. The antiradical capacity increases with the pH for all isomers until the hydrolysis limit (pH = 9.0). Square-wave voltammetry on boron-doped diamond electrode was used to determine the redox potentials of the phenolic betalains. Anodic potentials (E_p (mV, Ag *vs.* AgCl) 482 and 842 (BtPh-2-OH); 803 (BtPh-3-OH); 348 and 830 (BtPh-4-OH)) might indicate the oxidation of the phenolic portion as well as the 1,7-diazaheptamethine moieties. Control experiments with indicaxanthin (non-phenolic betalain of L-Pro) were performed (TEAC = 1.6 ± 0.1; E_p = 1044 mV (Ag *vs.* AgCl)). Results indicate that the phenol portion decreases the oxidation potential as well as increases the antiradical capacity.

Keywords: *betalain; antioxidant; natural pigment;*

Water, contaminants and food waste

O-171

SUSTAINING WATER RESOURCES IN AGRICULTURE

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Population growth and climate change will create widespread water stress worldwide within the next 40 years. The uneven distribution of freshwater globally, exacerbated by floods and increasing periods of drought, has a destructive impact on crop yields. Novel technologies have been developed to augment the world's finite freshwater systems but their applications each carry economic and/or ecological consequences. The objectives of this paper are to highlight key problems associated with regions undergoing agricultural stress and to present potential remediation. Three practical methodologies will be discussed: conservation, reclamation and desalination. Technologies for improving water retention are critical to conservation. The World Bank's 2006 report estimates that 25–30% of freshwater supply disappears, costing $14 billion annually to the global economy. Implementing sustainable drip irrigation conserves water effectively without incurring major capital investments. Recycling sewage water is a powerful tool for recuperating fresh groundwater. The Tel Aviv Dan Project, where 100% of municipal wastewater is recycled, has converted the Negev desert into arable agricultural land that is independent of drought; however the filtration and precipitation of salts has increased the salinity of the surrounding soils. Desalination produces water low in buffering capacity and thus needs to be remineralized both to reduce corrosion risks in the metal distribution pipes and to prevent stunted plant growth. Desalination is currently still highly energy intensive but reverse osmosis is far more ecofriendly than multi-flash distillation. Desalination becomes ecofriendly when linked to cogeneration with a power plant, where the cooling waters provide the diluent for brine disposal. Incompatible with sustaining resources for food is the growing of crops for biofuels. Instead research on cellulosic biomass or microalgae could provide more viable alternative energy sources. The feasibility of these methods has been demonstrated and further advances and implementation at a global scale require serious financial commitment.

Keywords: *renewable resources; water chemistry; biomass;*

Water, contaminants and food waste

O-172

ALTERNATIVE METHODS OF ADDING VALUE TO FOOD WASTE

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[1] *University of York, Department of Chemistry, York, United Kingdom*

Food waste is one of the most abundant sources of carbon on the planet with millions of tonnes generated from both the manufacturing process and dinner table. The Green Chemistry Group investigates a variety of methods by which these wastes can be converted into chemical products and in turn disposal costs into profits. From food waste a whole range of materials and products can be created ranging from high value platform molecules for conversion to pharmaceuticals, to materials, fermentable sugars and commodity chemicals. This presentation will present 3 cases studies from the Green Chemistry Group in this field.

Double Green Ltd and University of York won the Innovator10 Award. The company, who process high fat food wastes into biodiesel, developed a new technology for the use of glycerine, a co-product from biodiesel production, in various applications, including the generation of biogas. The work contributed to the characterisation of glycerin at different stages of production as well as the development of protocols for the synthesis of added value chemicals from glycerine.

Orange juicing is carried out worldwide and generates 50% waste from the juicing process, current best practice is to use the waste as animal feed, burn or turn into the land. Application of microwave assisted hydrothermal treatment of the orange peel waste can be used to extract valuable chemicals such as limonene and materials such as pectin and cellulose. The system can also be used to perform further downstream chemistry on the chemicals in-situ.

By integration of clean chemical technologies numerous higher value products can be generated from agricultural residues. Supercritical solvent can be used to extract cosmetic waxes, the straw can be directly converted to furniture boards and microwave technology can be used to generated energy products and chemicals.

Keywords: *Food waste; Biorefining;*

Sustainable food production – II

O-173

‘THOUGHT FOR FOOD’: CHEMISTRY AS THE BRIDGE BETWEEN THE MOLECULAR AND THE GLOBAL

J. C. HANEKAMP[1]

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Food is chemistry. A familiar remark that nevertheless has far-reaching consequences when viewed from the regulatory emphasis on antibiotics, pesticides, contaminants, and other so-called man-made molecules. Food then, in the public eye, seems nothing other than natural produce that has diminished nutritional value because of man-made contamination. That the chemistry of antibiotics, pesticides and the like has greatly improved food accessibility, reduced crop losses, and tackled many a disease that has its source in food seems forgotten in a world of ostensible nutritional and financial affluence. Not to get bogged down in a polarised debate, we want to address (**i**) the chemistry of food; (**ii**) sources of regulated chemicals; (**iii**) profiles of risk; and precaution (**iv**) a regulatory future for the globe. Concisely, as chemists we can bridge the chasm between the molecular and the global nature of food production and consumption.

Keywords: *Chemistry; Food; Antibiotics; Risk; Precaution;*

Sustainable food production – II

O-174

MATHEMATICAL MODELS: A KEY TOOL IN SUSTAINABLE FOOD PRODUCTION

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Manufacture efficiency, food quality change, shelf-life and food demand management are aspects of the food chain which are amenable to the application of mathematical models. Interestingly, these different aspects illustrate different types of mathematical modelling (i.e., kinetic, sequential, probabilistic, and self-learning) which will be discussed alongside their potential as predictive tools. Thus, this lecture will aim to demonstrate the applicability of mathematical modelling in this context and its accessibility to those involved in food production.

Sustainable food production – II

O-175

EFFECT OF HIGH HYDROSTATIC PRESSURE ON BIOGENIC AMINE FORMATION IN FERMENTED FOODS

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[3] *Corvinus University of Budapest, Department of Microbiology and Biotechnology, Budapest, Hungary*

Biogenic amines (BAs) are present in many foods, mainly in fermented products. Biogenic amines in food have great interest from both health protection and food quality control aspects. Consumption of food containing high quantities of BAs is responsible for many pseudo-allergic food related reactions and increased amounts of BAs are indicators of poor microbiological quality of the food.

Food scientists and the food industry made efforts to find and develop techniques to reduce or to prevent formation of BAs in food. The most implicated food group concerning high biogenic amine contents is fermented food.

The aim of this work was to study the effect of high hydrostatic pressure treatment (HHP) on the formation of BAs during production and storage of cheese and sausages.

Samples were pressurized at 500 MPa for 10 mins, total viable cell count (TVC) was determined on TPC agar and biogenic amine analysis was carried out by an automatic amino acid analyzer.

The HHP treatment reduced the level of TVC by 3.5-4 log cycles in cheese samples and by 1-3 log cycles in sausage depending on sample type (dry, semi-dry, extra thick sausage). The total biogenic amine content ranged between 3-207 μg/g in the controls and between 10-100 μg/g in the HHP-treated cheese samples. The total BA content of the extra thick sausage was the highest both in the control (118-35 μg/g) and in HHP treated samples (116-45 μg/g), followed by the dry sausage (c:103-46 μg/g; HHP:112-36 μg/g) and the semi-dry sausage (c:73-32 μg/g; HHP:84-13 μg/g).

HHP treatment improved the microbial stability of cheese and sausage and it was effective in the reduction of biogenic amine formation during storage.

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Keywords: *biogenic amines; high hydrostatic pressure; cheese; sausage; fermented food;*

New trends in organometallic chemistry – I

O-039

CONTROLLING AND UTILIZING THE CATALYTIC PRO- AND ANTI-OXIDANT PROPERTIES OF CORROLE METAL COMPLEXES

Z. GROSS [1]

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Heme containing enzymes are responsible for both the destruction and the utilization of reactive oxygen species (ROS), for protecting vital biomolecules against damage thereby and for biosynthesis, respectively. The most outstanding examples are catalases and peroxidases: they have the same prosthetic group (iron(III) protopophyrin IX), but the former disarm H_2O_2 by catalyzing its disproportionation and the latter utilize H_2O_2 as oxidant. One major challenge for using synthetic metal complexes for similar purposes is to gain control on the two conflicting aspects: their capability to both catalyze and prevent the oxidation of organic molecules by ROS.

Corrole and porphyrin metal complexes share many properties, but the trivalent states are more reactive and the high valent oxo-meal species are much more stable in the former case.[1] Several years ago we have started using these characteristics for several purposes: selective oxidation of organic molecules, small molecule activation, and decomposition of ROS in biological environments. Examples that will be presented include the enantioselective synthesis of an approved drug via biocatalysis,[2] clean four-electron electrocatalytic reduction of oxygen to water,[3] and the utilization of amphipolar metallocorroles as catalytic antioxidants in preclinical studies of diseases that are affected by ROS and reactive nitrogen species.[4]

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Keywords: *Catalysis; manganese; iron; antioxidants; porphyrin;*

New trends in organometallic chemistry – I

O-040

CATALYTIC POTENTIAL OF RUTHENIUM NANOPARTICLES INTERCALATED IN HECTORITE FOR SELECTIVE HYDROGENATION REACTIONS

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Benzene ruthenium(II) aqua complexes can be reduced in water or alcohols to give ruthenium(0) nanoparticles, the size of which varies from 2 to 50 nm depending on the reaction conditions. These nanoparticles can be stabilized by intercalation into layered clays such as hectorite (idealized cell formula $Mg_{5.5}Li_{0.5}Si_8O_{20}(OH)_4Na \cdot n\ H_2O$). Thus, ruthenium(0) nanoparticles are intercalated in hectorite by ion exchange of sodium against $[(C_6H_6)Ru(H_2O)_3]^{2+}$ cations between the anionic layers, followed by reduction with molecular hydrogen.[1, 2]

$$n\,[(C_6H_6)Ru(OH_2)_3]^{2+} + 7n\,H_2\ Ru_n + 2n\,H_3O^+ + n\,H_2O + n\,C_6H_{12}$$

Hectorite-supported ruthenium(0) nanoparticles proved to be highly active for the catalytic hydrogenation reactions. Thus, benzene can be hydrogenated to give cyclohexane under mild conditions (50°) with turnover frequencies up to 6500 cycles per hour.[2]

Highly selective hydrogenation reactions, catalyzed by nanoRu@hectorite under mild conditions, will be discussed: Furfuryl alcohol from renewable sources can be cleanly converted into tetrahydrofurfuryl alcohol,[3] a green solvent with a potential of fuel additive. The hydrogenation of α,β-unsaturated ketones gives exclusively the corresponding saturated ketones without reduction of the C=O function,[4] and the hydrogenation of quinoline yields selectively 1,2,3,4-tetrahydroquinoline. After a catalytic run, the nanoRu@hectorite catalyst can be recycled and reused without loss of activity and selectivity.

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Keywords: *Hydrogenation; Nanoparticles; Ruthenium;*

New trends in organometallic chemistry – I

O-041

IODIDE ACTIVATION OF COORDINATED WHITE PHOSPHORUS: FORMATION AND TRANSFORMATION OF 1,3-DIHYDRIDE-2-IODIDECYCLOTETRAPHOSPHANE

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The activation of elemental phosphorus mediated by transition metals represents a still challenging task that has been widely explored in the last decades.[1] Our group has found that the intact P_4 molecule may be bound to ruthenium fragments and that its reactivity, according to the electronic and/or steric requirements of the metal fragments, is significantly modified with respect to the free molecule. In particular the coordinated molecule undergoes easily dismutation in the presence of water to yield phosphanes [PH_3,[1]P_2H_4, [2]P_3H_4OH[3] and $P_4H_3(OH)_3$[4]] and oxoacids; the former being stabilized through coordination to ruthenium fragment(s) which, therefore, promote both the reactivity of the coordinated P_4 and the stabilization of the hydrolysis products, practically unknown as free ones.[5]

Here we report that the nucleophilic addition of I_2 to P_4 coordinated to two $CpRu(PPh_3)_2$ fragments affords a monocation of formula $[\{CpRu(PPh_3)_2\}_2(\mu^{1:3},h^{1:1}\text{-}P_4HI_2)]^+$ containing the 1,3-dihydride-2-iodidecyclotetraphosphane coordinated to two ruthenium fragments; the reactive $P_4H_2I^-$ anion easily dissociates iodide to yield the bicyclotetraphosphane, P_4H_2, which in turn undergoes dismutation in the presence of water to yield quantitatively the triphosphane, P_3H_5, and phosphorous acid, H_3PO_3. Both the bicyclotetraphosphane and the triphosphane, which are unknown as free ones, are stabilized through double metallation to yield the new compounds $[\{CpRu(PPh_3)_2\}_2(\mu^{1:3},h^{1:1}\text{-}P_4H_2)]OTf_2$ and $[\{CpRu(PPh_3)_2\}_2(\mu^{1:3},h^{1:1}\text{-}PH_2PHPH_2)]OTf_2$, respectively.

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Keywords: *White phosphorus; Activation;*

New trends in organometallic chemistry – I

O-042

REACTIONS OF A PHOSPHINITO BRIDGED DIPLATINUM(I) COMPLEX WITH COINAGE METAL ELECTROPHILES

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We have recently described the synthesis of the complex $[(PHCy_2)Pt^1(m\text{-}PCy_2)\{k^2P,O\text{-}m\text{-}P(O)Cy_2\}Pt^2(PHCy_2)]$ (*Pt-Pt*) (**1**), the first unsymmetrical phosphinito bridged Pt(I) species.[1] The phosphinito bridge differentiates the charge distributions on the two platinum atoms as confirmed by NMR spectroscopy ($d_{Pt(1)}$ = -4798 ppm, $d_{Pt(2)}$ = -5207 ppm) and DFT studies. Complex **1** shows a rich chemistry as it reacts with nucleophiles [$PHCy_2$, PCy_3, $P(S)HCy_2$],[2] protic species HX [$P(OH)Cy_2$, PhSH, HF, HCl, HBr, HI, HBF_4],[3, 4] and small molecules such as H_2.[5] Recently, we started investigations on the reactivity of complex **1** towards Au and Ag based electrophiles.

In this communication, it will be shown that, differently from the isolobal H^+ (which attacks the phosphinito oxygen and migrates onto the Pt-Pt bond),[3] the $[Ag(PPh_3)]^+$ electrophile attacks complex **1** selectively to the Pt^2-mP bond to afford the cationic cluster $[(PHCy_2)Pt^1(m\text{-}PCy_2)\{k^2P,O\text{-}m\text{-}P(O)Cy_2\}Pt^2\{m\text{-}Ag(PPh_3)\}(PHCy_2)]^+$ (*Pt–Pt*) (**2**$^+$) in which the $[Ag(PPh_3)]^+$ moiety bridges the mP-Pt^2 bond. Analogous reactivity is observed also when phosphane free electrophiles such as AgOTf, $AgBF_4$, $AgClO_4$ and AgCl are used. Moreover, the reactivity of **1** towards Au(I) electrophiles such as AuCl and $[Au(PPh_3)Cl]$ was dependent on the reagent and on the experimental conditions.

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Keywords: *Platinum; silver; gold; Phosphane ligands; Bridging ligands;*

New trends in organometallic chemistry – II

O-043

TRIAZOLE AND TETRAZOLE FE(II) COORDINATION COMPOUNDS EXHIBITING SPIN CROSSOVER.

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Triazole and tetrazole ligands are known to provide Fe(II) complexes the ideal range of ligand-field strength for the occurrence of spin crossover (SCO)[1], a stimuli-induced change of spin from a ground state low spin state (LS, $S=0$ in the case of Fe(II)) to a metastable high spin state (HS, $S=2$ here). In these systems, small synthetic variations in organic substituents or counteranions are means to tailor the SCO, either its temperature range or its cooperativeness in the solid-state, as well as to design nanostructures or soft matter phases.

This contribution will first illustrate such tuneability with recent advances based on triazole-based one-dimensional coordination polymers, with a focus on physical gels and liquid crystalline SCO materials[2]. Using these materials, we will also show that IR spectroscopy is a powerful tool to monitor the SCO, induced either thermally or through applied pressure at room temperature.

In a second part, the structural and magnetic properties of a new family of complexes $[Fe(mtz)_6](MX_4)_2$ (mtz = 1-methyl-tetrazole, M = Fe(III) or Ga(III), X = Cl or Br) will be presented. They represent the first SCO compounds with paramagnetic tetrahalo anions[3]. These latter implement ferromagnetic interactions and magnetic order at lower temperatures, in coexistence with the SCO, thus providing with original two-component multi-functional materials.

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Keywords: *Spin crossover; Iron; Magnetic properties; Metallomesogens; N ligands;*

New trends in organometallic chemistry – II

O-044

BIMETALLIC MOLECULAR CARBONYL CLUSTERS CONTAINING INTERSTITIAL CARBIDE ATOMS: STRUCTURAL FEATURES AND PHYSICAL PROPERTIES

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Much attention has been devoted in recent years to metallic nanoparticles and colloids from both a fundamental and applicative point of view.[1] Nonetheless, some major drawbacks remain due to the fact that they still are collections of species differing in sizes, shapes and compositions. Therefore, only average properties can be determined. Conversely, large molecular metal clusters are perfectly defined in composition and all structural details, and enter in the field of nanomaterials from the lowest limit.[2]

Herein, we describe some new nanometric bimetallic molecular carbonyl clusters stabilised by interstitial carbide atoms. The comparison of the structures of different Co-Ni, Co-Pd and Co-Pt carbido clusters shows the tendency, depending on the nature of the metals, to give species with complete, partial or none segregation of the two metals. Moreover, the extra stability of these molecular clusters allows the development of some interesting physical properties. For instance, paramagnetism in the even electron $[Co_8Pt_4C_2(CO)_{24}]^{2-}$ has been unequivocally demonstrates *via* SQUID and ESR measurements.[3]

In addition, electrochemical experiments show the tendency of larger clusters to undergo several reversible redox processes, as exemplified by $[H_{6-n}Ni_{22}Co_6C_6(CO)_{36}]^{n-}$ (n = 3-6). The polyhydride nature of these species will be presented as well. Finally, the robustness of molecular polycarbide clusters containing labile ligands makes them good candidates as nanometric building blocks for self-assembly.

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Keywords: *Cluster compounds; Carbonyl ligands; Nanoparticles; Structure elucidation; Carbides;*

New trends in organometallic chemistry – II

O-045

TAILOR-MADE PHOTOSENSITIZED POLYOXOMETALATES; TOWARDS THE DEVELOPMENT OF DEVICES FOR PHOTOCUMULATIVE ELECTRON TRANSFER

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Polyoxometalates (POMs) form a remarkable class of well-defined nanoclusters with an unmatched diversity of structures and properties.[1] They receive considerable interest because of their wide range of applications in many fields such as analytical chemistry, catalysis, materials science, or even medicine.[2] An important property of POMs is their ability to reversibly accept and release specific numbers of electrons under minor structural rearrangement. Therefore, POMs are attractive candidates for the development of photochemical devices aiming at photocumulative electron transfer. In this context, we recently reported the synthesis of inorganic/organic POM-based hybrids in which the POM is covalently connected to different types of photoactive antenna (pyrene, carbocyclometalated ruthenium and iridium complexes).[4–6] We herein describe the synthetic strategy of covalent attachment of these organic and organometallic chromophores to organo-silyl or organo-tin POM-based derivatives via Sonogashira couplings. The electronic and photophysical properties of the resulting hybrids will be presented, including transient absorption spectroscopy, which in some cases indicates the formation of unprecedented long-lived charge separation states.

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Keywords: *Polyoxometalate; Photochemistry; Electron transfer;*

New trends in organometallic chemistry – III

O-046

C-C BOND FORMING REACTIONS AT BRIDGING LIGANDS IN DIIRON COMPLEXES

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Interest toward iron mediated bond forming reactions has grown exponentially in recent years as consequence of increased attention to sustainability, and interest in replacing toxic and expensive metal catalysts with more cost-effective and benign transition metal compounds. In this growing effort aimed at new sustainable synthetic methodologies, diiron complexes can play a distinctive role in that they combine advantages associated to iron with those due to the presence of two adjacent metal centres. These include possible cooperative effects and multisite coordination of bridging organic fragments, which frequently results in peculiar reactivity patterns. A most relevant example of activation by diiron compounds is given by natural metallo-enzymes [FeFe] hydrogenases, which have inspired extensive investigation in the design of new sustainable energy process. However, diiron complexes might provide reasonable alternatives to precious metals in other research areas, such as C-C bond formation. Our report focuses on C-C bond forming reactions occurring at the at bridging hydrocarbyl ligands X (X = carbyne, vinylcarbene, vinyliminium etc.) in diiron complexes of type $[Fe_2(m\text{-}X)(m\text{-}CO)(CO)_nCp_2]$. (n = 1, 2) A few selected examples will be presented, including:

i) insertion of alkynes into the metal-carbyne carbon bond; **ii**) nucleophilic addition at vinyliminium ligands (non-conjugated additions); **iii**) activation of aC-H and gC-H in bridging vinylimiums; **iv**) 1,3 dipolar cycloadditions, and [3+2] cycloadditions of bridging C3 ligands with alkynes; **v**) [3+2+1] cycloadditions of alkynes, CO and **vi**) -vinylcarbenes; alkyne incorporation by enyne metathesis.

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Keywords: *diiron complexes;*

New trends in organometallic chemistry – III

O-047

SOL-GEL COORDINATION CHEMISTRY: A NOVEL APPROACH TO INCORPORATE CHEMICAL FUNCTIONALITY IN POROUS MATERIALS

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A novel methodology to incorporate chemical functionalities into the framework (not on the surface) of porous materials has been developed via co-condensation of a silica precursor (typically a silicon alkoxide) and trialkoxysilanes bonded to different chemical moieties. Following this strategy, different functionalities, including metal nanoparticles,[1] organometallic compounds and metal complexes[2–3] as well as inorganic clusters,[4] have been effectively incorporated into the framework of the mesoporous silica and organosilica materials. This approach has been recently extended to titania and other metal oxide supports. A critical overview of the various strategies on this novel strategy and its main advantages over more traditional functionalization method, like grafting, can be found elsewhere [5].

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Keywords: *sol-gel processes; mesoporous materials; nanoparticles; complexes; condensation;*

New trends in organometallic chemistry – III

O-048

STRUCTURE AND REACTIVITY OF FISCHER BISCARBENE COMPLEXES

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The application of alkoxycarbene ligands as active synthons in template reactions in organic synthesis and catalysis is mainly focused on monocarbene complexes.Very few larger assemblies of carbene units and metal fragments (polymers, dendrimers, metal organic frameworks, etc.) have been reported. Hence, multimetal carbene and multicarbene metal complexes are becoming increasingly more important.[1, 2]

Thiophenes with two alkoxycarbene ligands in chelate rings and attached to group 6 transition metals were synthesized after activating atypical positions by lithium-halogen exchange reactions or by selectively blocking activated positions on the thiophene ring. The carbene carbon atoms in the α-positions differed in their reactivity from those in the β-positions of thiophene.[3]

Biscarbene complexes expose activated sites and can be used as precursors to synthesize modified monocarbene complexes or shed light on intermediates involving the metal-carbon double bond during conversions or formation of reactive intermediates.[4]

Piggybacking alkoxycarbene complexes as substituents of amine and phosphine ligands into the coordination sphere of transition metals was successfully accomplished for group 6 to 10 transition metals. Structural features and the availability and potential reactivity of these carbene-containing complexes in template reactions were investigated. Alternatively, this method can be used to import carbene complexes in larger assemblies of group 7 and 10 transition metalorganic frameworks.

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Keywords: *Carbene; Structure; Reactivity;*

New trends in organometallic chemistry – III

O-049

METAL-CATALYZED, METAL-PROMOTED AND METAL-FREE FUNCTIONALIZATION OF ALKANES

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On account of their inertness, alkanes are normally used as fuels, and their selective conversion into functionalized organic compounds is a current challenge, with significance in search for alternative raw materials. Of particular meaning would be the development of systems operating under mild and green conditions.

Results obtained by the author's Group on the following reactions will be described:

i- Peroxidative oxidations of alkanes to alcohols and ketones, catalyzed by metal complexes;

ii- Metal-free and metal-promoted hydrocarboxylations of alkanes to carboxylic acids, with water as hydroxylating agent;

iii- Metal-catalyzed alkane carboxylations to carboxylic acids.

Some of systems feature the highest reported catalytic activities in the field.

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Keywords: *Alkanes; Carboxylation; Oxidation; Peroxides; Alcohols;*

Inorganic/bioinorganic reaction mechanisms – I

O-176

GREEN MECHANISTIC CHALLENGES OF CATALYSIS VIA TAML IRON(IV)- AND IRON(V)OXO SPECIES (TAML=TETRAAMIDOMACROCYCLIC LIGAND)

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Iron(III) complexed to four deprotonated amide nitrogens of *t*etra*a*mido*m*acrocyclic *l*igands (TAML) are unique catalysts for various green oxidations by hydrogen peroxide. Mechanistically, the catalysts have features typical of peroxidase and monooxygenase enzymes. Two generations of TAML ligands have been introduced using a rational design approach. In aqueous media, the catalyst iron reaches the oxidation state of IV in the presence of peroxides, whereas the oxidation state of V is reachable in a more than 95% yield in organic solvents. Therefore the reactivity of the TAML iron(V)oxo species have directly been investigated with respect to several target molecules. The iron(V)oxo units are normally by four orders of magnitude more reactive than the iron(IV)oxo analogues. In this lecture, diverse mechanistic aspects of catalysis by the iron TAML compounds in water will be discussed with the emphasis at the catalysts of second generation together with the recent kinetic results on the reactivity of iron(V)oxo TAML derivatives generated at lower temperatures in acetonitrile as a solvent. The two closely related topics should highlight broad prospects of the catalysts in green and sustainable environmental chemistry.

Keywords: *iron; catalysis; green chemistry; kinetics; mechanism;*

Inorganic/bioinorganic reaction mechanisms – I

O-177

PHYSICOCHEMICAL STUDIES AND ANTICANCER POTENCY OF RUTHENIUM(P-CYMENE) COMPLEXES CONTAINING ANTIBACTERIAL QUINOLONES

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Quinolone antibacterial agents are used in clinical practice for nearly fifty years. It is known that metal ions coordinate to quinolones and some complexes exert biological activity.[1] The synthesis and study of metal complexes with drugs used in clinical practice, which may exhibit synergistic activity, have attracted much attention in last years.

Recently organometallic ruthenium complex of quinolone ofloxacin (oflo), [(η^6-p-cymene)RuCl(O,O-oflo)] (**1**), was isolated and characterized.[2] In this "piano-stool" complex, quinolone is bidentately coordinated to the metal through the ring carbonyl and one of the carboxylic oxygen atoms. Interactions of this complex with DNA were studied by different spectroscopic methods and atomic force microscopy. Later, analogous compounds of the quinolones nalidixic acid (**2**) and cinoxacin (**3**) were synthesized, and their properties were compared to those of **1**.[3] All compounds undergo a rapid ligand exchange reaction from chlorido to aqua species. In contrast, **2** and **3** are significantly more stable than **1** and undergo minor conversion to an unreactive species. In the presence of human serum albumin **1**–**3** form adducts within 20 minutes of incubation. With guanosine 5'-monophosphate rapid reactions yielding adducts via its N7 atom were observed, illustrating that DNA is a possible target for this compound class. A moderate capacity of inhibiting tumor cell proliferation in vitro was observed for **1** in CH1 ovarian cancer cells, whereas **2** and **3** turned out to be inactive.

Acknowledgement: *Financial support from the Slovenian Research Agency through project J1-4131 is gratefully acknowledged.*

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Keywords: *Bioinorganic chemistry; Ruthenium; Antibiotics; Biological activity;*

Inorganic/bioinorganic reaction mechanisms – I

O-178

REACTIVITY OF NI(0)-COMPLEXES TOWARDS ALKENES AND ALKYNES

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In regard to the application of Ni(0) compounds as catalysts in organic synthesis[1] there is high interest in better understanding of the reactivity of these complexes. Detailed kinetic investigations have been performed previously on substitution reactions of [Ni(bipy)COD] (bipy = 2,2'-bipyridine, COD = 1,5-cyclooctadiene) by Schindler and co-workers.[2] Furthermore, de Meijere and co-workers have synthesized and characterized bicyclopropylidene ***bcp***[3] and dicyclopropylacetylene ***dcpa***[4] and their reactivity. Based on this background it seemed interesting to investigate the according Ni(0) complexes of these compounds. Both complexes, [Ni(bipy)bcp] and [Ni(bipy)dcpa] were structurally characterized. The formation of these complexes could be investigated by UV-VIS spectroscopy using "stopped-flow" techniques.

Despite the negative entropy of activation a dissociative mechanism was proposed for the reaction of [Ni(bipy)COD] with *bcp* according to previous kinetic studies with other olefinic ligands.

The reaction of [Ni(bipy)(COD)] with *dcpa* is slower compared with *bcp*. Nevertheless, it was not possible to obtain acceptable fittings to single-exponential functions for all concentrations applied over the selected temperature range. Therefore, the reaction with another alkine, dimethoxybutyne ***dmbu*** was investigated. Detailed kinetic studies of this reaction will be presented.

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Keywords: *Nickel; alkenes; alkynes; UV/Vis spectroscopy;*

Inorganic/bioinorganic reaction mechanisms – I

O-179

NO AND CO RELEASING MATERIALS

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Nitric oxide (NO) and carbon monoxide (CO) are messenger molecules in the human body.[1] NO- and CO-releasing materials (NORMAs & CORMAs) can act as gasotrans-mitter delivering devices in therapy; toxic metabolites after gas release are kept in the matrix. NO and CO photodonors use light as a trigger allowing the accurate control of site, timing and dosage.[2] Here we report the concept of embedding water-insoluble, photoactive NO and CO metal complexes into nanofibrous polymer non-wovens.[3]NO and CO release is performed by light stimu-lation of the high surface area materials. For the generation of NORMAs, novel rutheniumnitrosyl complexes $\{RuNO\}^6$ have been synthesized.[4] For the CORMAs, $Mn_2(CO)_{10}$ and $Fe(CO)_5$ were used.[5] These metal complexes were non-covalently embedded into polylactide non-wovens by electrospinning. Identity of the metal complexes was retained in the electrospinning process. Leaching of the metal complexes out of the polymeric matrices into water was negli-gible due to their water insolubility (verified by AAS, ICP-MS, UV/Vis). Cytotoxicity tests with 3T3 mouse fibro-blasts revealed a very low mortality rate. Irradiation at $\lambda=366$ nm (UV-A, 3 mW/cm^2) in water, using Anslyn's fluores-cent NO assay, showed a significant phototriggered NO release from the non-wovens.[4] Rapid CO release from CORMAs was detected by the myoglobin assay and vibrational spectroscopy.[5]

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Keywords: *Nanostructures; Ruthenium; Polymers; Nitrogen oxides; Immobilization;*

Inorganic/bioinorganic reaction mechanisms – II

O-180

STRUCTURAL AND SPECTROSCOPIC CHARACTERIZATION AND REACTIVITIES OF METAL-OXYGEN INTERMEDIATES

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Dioxygen is essential in life processes, and enzymes activate dioxygen to carry out a variety of biological reactions. One primary goal in biomimetic research is to elucidate structures of reactive intermediates and mechanistic details of dioxygen activation and oxygenation reactions occurring at the active sites of enzymes. During the past decade, we have been studying the chemical and physical properties of various reactive intermediates in oxygenation reactions, such as high-valent iron(IV)-oxo complexes of non-heme ligands in oxo-transfer and C-H activation reactions, metal-peroxo complexes in nucleophilic reactions, and metal-superoxo complexes in electrophilic reactions. In this presentation, I will present our recent results on the synthesis and structural and spectroscopic characterization of mononuclear nonheme metal-dioxygen intermediates. Their reactivities in electrophilic and nucleophilic oxidation reactions will be discussed as well.

Keywords: *bioinorganic chemistry; enzyme models; reactive intermediates;*

Inorganic/bioinorganic reaction mechanisms – II

O-181

NOVEL HYDROQUINONATE/P-SEMIQUINONATE VANADIUM(IV/V) BIOINORGANIC MODELS, EFFECTIVE CATALYSTS FOR THE SELECTIVE REDUCTION OF O_2 TO H_2O_2

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Transition metal centered reductive O_2 activation is a fundamental process in various O_2 oxidation reactions and physiological O_2 metabolism. Enzymes exhibiting in the active site two redox centers one inorganic and one organic, such as galactose oxidase and copper amine oxidase, utilizes O_2 to oxidize organic substrates releasing H_2O_2. Synthesis of model compounds that will mimic this activity is of particular interest because of the applications can be found in the use of O_2 as green oxidant and in the facile on-site production of H_2O_2 which is also a powerful green oxidant and can be used for clean energy storage. The last few years, we have pursued the synthesis of two redox center metal bioinorganic model complexes and stabilization of *p*-semiquinonate radicals. In particular, vanadium complexes because vanadium based enzymes and compounds utilize O_2 and/or H_2O_2, catalyzing oxidative C-H activation, epoxidation and alcohol oxidation reactions. Although, O_2 is the most preferable oxidant, the more reactive peroxides are used in combination with the vanadate catalysts. Paramagnetic vanadyl compounds are expected to be better choice for overcoming the spin restrictions and activate O_2 than vanadates. In this work we have developed dinuclear vanadyl hydroquinone/p-semiquinonate complexes that catalytically reduce O_2 producing H_2O_2. Although these complexes have been isolated in very acidic conditions with excess of chlorides, crystallographic characterization showed that the positive charge of the semiquinonate compound is neutralized with hydroxide anions. UV-Vis, electrochemistry and EPR support that between pH 2.2 and 2.8 the V^{IV}-semiquinonate exhibit a slow reversible pH metal to ligand electron transfer towards the formation of hexanuclear V^{IV}-O-V^{V} bridged hydroquinonate species. The two redox center vanadyl complex is a very effective catalyst for the selective reduction of O_2 to H_2O_2 and the mechanism of this activation was investigated. Financial support from RPF and European Structural Funds, ANABAUMISI/PAGIO/0308/32.

Keywords: *Vanadium; Reaction mechanisms; O-O activation; Bioinorganic chemistry; Redox chemistry;*

Inorganic/bioinorganic reaction mechanisms – II

O-182

APPARENT OR REAL? THE INTERESTING CASE OF WATER EXCHANGE REACTIONS ON $[ZN(H_2O)4(L)]^2+•2H_2O$ (L = NITROGEN DONOR LIGANDS)

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Detailed knowledge of the reactivity of the Zn(II)-cation is a necessity since Zn^{2+} is one of the most important ions in bioinorganic chemistry and plays a crucial rule in catalysis.[1] While solvent exchange reactions are the most fundamental substitution processes that a solvated metal ion can undergo and do not necessarily lead to a chemical conversion, they contribute fundamentally to our understanding of reactivity and substitution mechanisms. Experiments will lead to knowledge about reactions under realistic conditions, in contrast to quantum chemical calculations that permit detailed investigations unbiased by external effects. Earlier work reported I_d- or D-mechanisms for H_2O exchange at six-fold coordinated $[Zn(H_2O)_6]^{2+}$.[1]

In the present work we found for all ligands (L) in five-fold coordinated $[Zn(L)(H_2O)_4]^{2+}$ an associative type of water exchange mechanism, depending on the ligand (L) and its properties, *e.g.* pK_a values, proton affinity, *etc.* focusing on ligands with N-donors (*e.g.* HCN, py, NH_3, *etc.*).[2,3] The complete reaction consists of an associative binding of one H_2O from the second coordination sphere leading to a six-coordinate intermediate $[Zn(H_2O)_5(L)]^{2+}\cdot H_2O$, followed by the dissociation of a water molecule to reach the product state $[Zn(H_2O)_4(L)]^{2+}\cdot 2H_2O$. For a real water exchange reaction to occur, two different transition states have to be included, otherwise only an apparent water exchange reaction takes place. For the water exchange reaction in $[Zn(H_2O)_4(L)]^{2+}\cdot 2H_2O$ nearly iso-energetic *cis*- and *trans*-orientated transition states are crossed.[4]

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Keywords: *Reaction mechanisms; Zinc; Quantum Chemistry;*

Inorganic/bioinorganic reaction mechanisms – III

O-183

CATALYTIC TRANSFORMATION OF SUPEROXIDE, NITRIC OXIDE, PEROXYNITRITE AND HYDROGEN SULFIDE FOR MEDICAL AND INDUSTRIAL APPLICATIONS

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Superoxide, nitric oxide, peroxynitrite and hydrogen sulfide are small inorganic species that have diverse roles in biological systems. On the one hand they are toxic species involved in different pathologies but on the other hand they are signaling molecules with important physiological effects. Metal centers are one of their first targets in biological milieu, however the elementary reaction steps behind these interactions, which can both have stoichiometric and catalytic nature, are still unrevealed. New fundamental insights into these interactions and their potential pharmaceutical and catalytic applications will be presented.

Inorganic/bioinorganic reaction mechanisms – III

O-184

A FRET ENZYME-BASED PROBE FOR MONITORING HYDROGEN SULFIDE

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Hydrogen sulfide (H_2S) is among the oldest and simplest of molecules whose reaction chemistry has very recently attracted attention from several research groups. In particular, recent efforts are mostly devoted to implement sensitive and selective detection techniques to monitor the distribution and function of this molecule in complicated biological systems.[1] For hundreds of years it has been known solely as a harmful gas.[2] More recently, H_2S has emerged as the "third gaseous transmitter" in biology.[3]

Recently we and others proposed an innovative method to make proteins suitable for sensing applications. The scheme builds on the translation of the binding event occurring at the enzyme cofactor binding-site into a change in the emission of a fluorescent probe covalently attached to the protein through a Förster Resonance Energy Transfer (FRET) mechanism.[4, 5]

In the present contribution we show that fluorescently labeled cobalt peptide deformylase (Co-PDF) can be efficiently used as a FRET-based sensing device for H_2S. DFT calculations were performed to gain insight into the characteristics of the coordination adduct between H_2S and Co-PDF. Mercaptoethanol coordination to Co-PDF was verified by X-ray crystallography. We also report the crystal structure analysis of the monohydrogensulfide Co-PDF complex as proof of our method in H_2S detection.

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Keywords: *biosensors; fluorescence;*

Inorganic/bioinorganic reaction mechanisms – III

O-185

NEW INSIGHTS INTO THE POLYMERISATION MECHANISMS FOR POLYPHOSPHAZENE PRECURSORS

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Polyphosphazenes, $[N=PR_2]_n$, represent one of the most versatile classes of inorganic polymers. The ability to tune the chemical and physical properties of these materials through the substituents R has enabled a broad range of promising applications.[1] Most of the synthetic methods to phosphazene polymers suffer from poor molecular weight control and the formation of broad molecular weight distributions. In 1995 the first example of the living polymerization route to polyphosphazenes was reported which involved the treatment of trichloro(*N*-trimethylsilyl)-phosphoranimine, $Cl_3P=NSiMe_3$, with PCl_5.[2] In contrast to other routes, this method allows the molecular weight of the polymer to be controlled by altering the monomer to initiator ratio to give polydichloro-phosphazenes in high yield with relatively narrow molecular weight distributions. Although the discovery of this living polymerization of $Cl_3P=NSiMe_3$ has permitted a range of synthetic advances, its mechanism has not been fully elucidated.

Based on recent results using model chemistry[3] we have now further investigated the mechanism of the PCl_5-initiated living polymerization of $Cl_3P=NSiMe_3$. These studies give interesting results and have shown that the polymerization process is much more complex than originally proposed.

Furthermore, the phosphite-initiated polymerization of bromophosphoranimine $BrMePhP=NSiMe_3$[4] has been investigated in more detail. It was found that alternative compounds to phosphites can act as much more active initiators.

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Keywords: *polyphosphazenes; mechanisms; polymerizations; main group chemistry;*

Inorganic/bioinorganic reaction mechanisms – III

O-186

REDOX REACTIONS OF THE PEROXOMONOSULFATE ION IN THE FERROIN/FERRIIN SYSTEM

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Peroxomonosulfate ion (oxone, HSO_5^-) is a strong, two-electron oxidant also used as an inexpensive and environmentally friendly agent in advanced oxidation procedures. Experiments involving oxone add valuable information to the study of reactive intermediates, may confirm mechanistic considerations regarding the autoxidation of various substrates and may explore important aspects of industrial applications.

This presentation reports a kinetic study on the reactions of oxone in the ferroin/ferriin system (the tris-1,10-phenanthroline complexes of Fe^{II} and Fe^{III}), which is frequently used for modelling the redox activity of biological compounds. A complex kinetic behavior was observed: the concentration of ferroin decreases in the first stage of the reaction; however, after reaching a minimum the concentration increases to a maximum and then decreases again. A similar behavior was described previously in the reaction of ferroin with Ce(IV).[1]

Detailed kinetic study and ESI mass spectrometry confirmed the formation of an 1:1 adduct between the reactants in the initial phase of the ferroin-HSO_5^- reaction.[2] The oxidation product, 1,10-phenanthroline-mono-N-oxide was identified in the reaction mixture with several methods (UV-Vis, ESI-MS, ^{1}H-NMR). The N-oxide has significant inhibiting effect: upon the addition of the N-oxide to the initial mixture, a slower consumption of ferroin was observed. A kinetic model was proposed for the reaction and independent measurements were carried out with ferriin which is also formed in the reaction.

Ferriin decomposes in strongly acidic solutions producing ferroin and 1,10-phenanthroline-mono-N-oxide. 1,10-Phenanthroline-mono-N-oxide has a slight autocatalytic effect on the decomposition and increases the rate of ferroin formation. We propose the formation of $Fe(phen)_3^{4+}$ as a minor intermediate in the overall process.[3]

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Keywords: *oxone; redox chemistry; reactive intermediate; AOP; reaction mechanism;*

Symposium on CO2 chemistry – I

O-306

CO_2 CAPTURE FROM FLUE GASES: EXISTING OPTIONS AND PERSPECTIVES

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Over the past 10-20 years, a variety of processes for capturing carbon dioxide from flue gases have been developed. In particular chemical absorption processes have meanwhile reached a level of maturity that these processes nowadays can be applied on an industrial scale.

The paper provides an overview over the most relevant technologies and focuses on some key performance figures and characteristics: purity of the processed streams, energy consumption, solvent circulation rates as well as emissions and product availability and process reliability are important parameters, when it comes to process selection.

In public discussion, chemical absorption processes are often criticized for their high energy consumption. With an entropy evaluation, the paper will show, where the thermodynamic minimum energy consumption will be, what level can be realized under reasonable boundary conditions and how this compared to today's technologies. The approach is independent on the type of process and can also be used to predict the separation efficiency of e.g. adsorption or membrane processes.

Atop, the latest developments to further improve the process performance of carbon dioxide absorption will be presented and some of the major challenges will be discussed.

Keywords: *Chemisorption; Absorption;*

Symposium on CO2 chemistry – I

O-307

CO_2 - INSERTION INTO SI-N-BONDS - A MECHANISTIC STUDY

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CO_2 may be used as starting material for chemical syntheses, e. g. for the synthesis of urea, methanol, and several carbonates. Hence, CO_2 is mainly used as a C1 source. One of the several methods known for the activation of CO_2[1] is the insertion into a main group or transition metal nitrogen bond.[2] Most of the literature focus on the reactions of Me_3SiCl with primary and secondary amines, e. g. using the TMS substituent as directing group in organic synthesis.[3] In contrast, we report here the use of Me_2SiCl_2 and a primary amine as starting materials for the synthesis of diaminosilanes $Me_2Si(NHR)_2$. Subsequent quantitative *bis*-insertion of CO_2 yields the corresponding di(alkylcarbamoyloxy)dimethylsilanes $Me_2Si(OCONHR)_2$.[4, 5]

Diaminosilanes of the type $(RHN)_2SiMe_2$, obtained from Me_2SiCl_2 and primary amines, were subjected to a double insertion of CO_2 at room temperature to afford the carbamoyloxysilanes. The latter reaction is exothermic and proceeds with very good yields. To gain further insight into the reaction mechanism of the CO_2 insertion, we performed DFT calculations with a simple model aminosilane, $Me_2Si(NHMe)_2$.[6]

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Keywords: *Insertion; Silicon; Amines; Carbon dioxide fixation; Density functional calculations;*

Symposium on CO2 chemistry – I

O-308

UNPRECEDENTED ALKYLZINC CARBONATE VIA BIO-INSPIRED ROUTE INVOLVING RZNOH AND CO$_2$

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Over the last decade, bio-fixation approaches for the CO$_2$ sequestration have received much attention because of their great environmental significance as well as very promising practical applications in materials chemistry.[1] This bio-inspired solution for chemical activation of CO$_2$ is mostly based on ZnOH type reaction systems patterned on active centre of carbonic anhydrase (CA).[2] However, despite numerous inorganic complexes investigated as CA mimics, the organozinc RZnOH compounds have not yet been investigated in this context.

Here we report on the activation of CO$_2$ by the model alkylzinc hydroxide[3] $(^t\mathrm{BuZnOH})_6$ (**1**) in the absence and presence of $^t\mathrm{Bu}_2\mathrm{Zn}$ as proton acceptor, and the isolation of the unprecedented dodecanuclear alkylzinc carbonate $[(^t\mathrm{BuZn})_2(\mu_5\text{-}\mathrm{CO}_3)]_6$ cluster (**2**). Compound **2** was fully characterized in the solid state by X-ray diffraction studies and the presence of the carbonate group is substantiated by CP-MAS ^{13}C NMR and IR spectroscopy. The ^{1}H NMR spectroscopic studies clearly indicate that the presence of an excess of $^t\mathrm{Bu}_2\mathrm{Zn}$ in the **1**/CO$_2$ reaction system greatly accelerates the proton transfer from an intermediate Zn(HCO$_3$) bicarbonate and significantly improves the reaction yield. Moreover, the existence of the reactive M-C bond in the reported complexes is a unique feature qualifying these systems for further post-synthetic modification in order to design of a new class of carbonate secondary building blocks for materials chemistry. Further biologically inspired studies on the reactivity of organozinc Zn–OH systems supported by organic ligands towards effective CO$_2$ bio-fixation and other small molecules are in progress.

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Keywords: *carbon dioxide; bio-fixation; zinc hydroxide; zinc alkyls; proton acceptor;*

Symposium on CO2 chemistry – I

O-309

MECHANISTIC INSIGHT FROM ACTIVATION PARAMETERS FOR THE REACTION OF A RUTHENIUM HYDRIDE COMPLEX WITH CARBON DIOXIDE IN CONVENTIONAL SOLVENTS AND AN IONIC LIQUID

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The reduction of carbon dioxide to a useable resource (fuel or otherwise) is a major goal in current chemical research. One possible way would be to use a hydride transfer reaction by which CO$_2$ will first be reduced to formic acid. The reaction rate of the reaction of a ruthenium hydride complex $(\mathrm{Ru^{II}(terpy)(bpy)H})^+$ (terpy = 2,2',6',2''-terpyridine; bpy = 2,2'-bipyridine) with CO$_2$ to form a formate adduct strongly depends on the solvent[1]. Detailed kinetic studies in conventional solvents (water, methanol and ethanol) and in the ionic liquid [emim][NTf$_2$] ([emim]=1-ethyl-3-methyl-imidazolium; [NTf$_2$]=bistrifluoromethylsulfonylamide) using stopped-flow methods were performed and second-order rate constants and activation parameters ($\Delta H^\#$, $\Delta S^\#$ and $\Delta V^\#$) were determined for the reaction in all solvents. The second-order rate constants correlate with the acceptor number of the solvent, whereas the activation parameters support the nature of the insertion mechanism of the reaction. The results in water, especially the activation entropy ($+14 \pm 2$ J K^{-1} mol^{-1}) and activation volume (-5.9 ± 0.6 cm^3 mol^{-1}), differ significantly from those found for the other solvents, underlining the importance of hydrogen bond formation in the transition state.

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Keywords: *reaction mechanisms; kinetics; insertion; carbon dioxide;*

Symposium on CO2 chemistry – II

O-310

CHEMICALS AND FUELS FROM CO_2: THE EXISTING BARRIERS TO EXPLOITATION

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The use of carbon dioxide (CCU) to produce chemicals and fuels through biotechnological, biological, chemical, photo-chemical and photo-electrochemical processes is nowadays considered a way to reduce its atmospheric loading. Time is now to step towards the “Artificial photosynthesis”. CCU can be advantageously integrated within the Carbon Capture-CC and Carbon Capture and Storage-CCS technologies for improving their economic costs.

Noteworthy, to use carbon dioxide means to reduce both the use of fossil C and the carbon dioxide emission into the atmosphere with the double benefit of preserving reserves and improving our environment.

In this paper, the possible uses of CO_2 as source of carbon for chemicals and fuels will be summarized. A deeper insight into the synthesis of organic acyclic carbonates will highlight the existing barriers to a full exploitation of the CO_2-based technology and will show how such barriers can be circumvented.

Symposium on CO2 chemistry – II

O-311

EXPERIMENTAL INVESTIGATIONS OF NONSTOICHIOMETRY FOR A SIMPLE CLATHRATE HYDRATE OF CARBON DIOXIDE

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The technologies using clathrate hydrates are promising as energy storage and environmental technologies. They are one of host-guest materials and include nonstoichiometric number of guest molecule within host water cages, and the contents of a guest substance could be varied depending on forming conditions. The technology using clathrate hydrates of carbon dioxide are expected to be the one for the carbon capture and storage. Therefore, the contents of CO_2 in clathrate hydrates, i.e., cage occupancies, are significant properties for industrial use. However, there was a difficulty to determine them correctly, based on diffraction measurements, due to the disorder of the CO_2 molecule positions in the hydrate cages. This paper reports an attempt to improve the experimental determination of cage occupancies for simple clathrate hydrates of CO_2. The powder X-ray diffraction (PXRD) measurement technique was applied to estimate the cage occupancies by the Rietveld method with the aid of the direct space method for clathrate hydrates [Takeya et al., J. Am. Chem. Soc., 2010]. The method allows to optimize guest-molecule positions in hydrate cages and to determine cage occupancies from powder samples. The hydrate samples were formed at the pressure over or nearly equal to the phase equilibrium pressure. The forming conditions were ranged in the temperatures from 274 K to 280 K and the pressures from 1.5 MPa to 3 MPa. Mass measurements for carbon dioxide and water were also performed in order to verify the data obtained from the PXRD measurements. The contents of CO_2 could be obtained on the basis of an absolute measurement technique. The pressure dependence for the small cage occupancy was clearly observed. The data of cage occupancies obtained in this study were compared with the experimental data and predictions reported in the literature, and discussion was made based on the comparison.

Keywords: *Clathrates; Carbon dioxide fixation; hydrates; Nonstoichiometric compounds; Inclusion compounds;*

Symposium on CO2 chemistry – II

O-312

CATALYTIC SYNTHESIS OF 2-HYDROXYMETHYL-OXAZOLIDINONES FROM GLYCEROL CARBONATE OR GLYCEROL AND UREA

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2-oxazolidinones are important heterocyclic compounds that find several applications in particular as antibiotics, pesticides, and in drug or fibers production. Industrially, 2-oxazolidinones are synthesized starting from amino alcohol and phosgene,[1] CO_2[2] or cyclic carbonates.[3] All such routes are affected by the formation of polymers, harsh reaction conditions and high cost. In this work, we report the synthesis of hydroxymethyl-2-oxazolidinones obtained reacting glycerol carbonate (GC) and urea or glycerol and urea. GC is a non toxic and easy biodegradable compound that can be prepared in high yields and at low cost under mild reaction conditions by glycerolysis of urea [4]. Such approach represents from one side a new application of GC or glycerol and from the other a new "green" route to oxazolidinones. γ -ZrP has been used as catalyst and we show that the modulation of the acid/base properties of the catalyst play a key role in the transformation of either substrate into 2-oxazolidinones. GC and urea in presence of non calcined γ-ZrP, at 20 Pa and 408 K react to afford 2-oxazolidinones with a selectivity close to 100% and a conversion of 21%. At 453 K the conversion of GC into 2-oxazolidinones increases but the selectivity decreases and new molecular products are formed. In absence of catalyst the reaction does not occur under the same conditions. The reaction conditions and the reaction mechanism have been investigated and will be discussed.

Acknowledgements: *The authors acknowledge funding from the EU Seventh Framework Programme (FP7/2007-2013) under grant agreement n° 241718 EuroBioRef.*

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Keywords: *2-hydroxymethyl-oxazolidinones; glycerol carbonate; heterogeneous catalysts;*

Symposium on CO2 chemistry – III

O-313

FIXATION OF CO_2 AS CARBONATES OF MAGNESIUM OR CALCIUM

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The fixation of CO_2 in (hydro-)carbonates brings together the goals of CO_2 emissions reduction, valorization or stabilization of waste streams and more sustainable or otherwise advanced chemical processing. While CO_2 mineral sequestration using the world's vast magnesium silicate resources was recognized as a CCS (carbon dioxide capture and storage) route in the early 1990s, most CCS efforts aim at underground storage of pressurized CO_2. Only recently the large-scale carbonation of minerals was again recognized as a serious alternative for underground storage as it gives leakage-free, permanent storage that won't require post-storage monitoring and seems to be applicable more widely. Moreover, it is suitable for trapping CO_2 from streams that contain oxygen as well, making it not only more versatile but also presents the option of removing the problematic and expensive capture step from the CCS process chain. Finally, uses for the significant amounts of solid (hydro-)carbonate product and by-products obtained are being recognized, ranging from land reclamation to specialized products. These increasingly patent-driven developments that define an overlap of CCS and CCU (carbon dioxide capture and utilization) shall be summarized here.

More developed and closer to commercial application are process routes that utilize CO_2 for the production of calcium carbonates including the highly valuable precipitated calcium carbonate (PCC). Roughly since year 2000 many calcium-containing by-products, residues and wastes are investigated for the potential to bind CO_2 which offers emissions reduction potential while reducing (costly) landfill and the use of natural resources. Slag residue from iron and steel-making or ashes from for example oil shale combustion are important examples of calcium-based CCU methods addressed in this presentation.

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Keywords: *CO2; mineral; carbonation; magnesium; calcium;*

Symposium on CO2 chemistry – III

O-314

PHOTO-ELECTROCHEMICAL NADH REGENERATION FOR ENZYMATIC CARBON DIOXIDE REDUCTION TO METHANOL: EFFICIENT METAL-MODIFIED SEMICONDUCTOR ELECTRODES

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The enzymatic reduction of carbon dioxide into methanol through the dehydrogenase enzyme cascade $F_{ate}DH$, $F_{ald}DH$ and *ADH* represents a unique process for CO_2 reduction as it occurs under very mild conditions (water, 37°C, pH = 7) and with optimal yield and selectivity (close to 100%).[1] Nevertheless there still is a limitation associated with the consumption of the cofactor NADH that is converted into the oxidized form NAD^+. Enzymatic, chemical and photochemical approaches have been attempted,[2] but over all these strategies electrochemical regeneration is considered the most attractive one.[4]

Herein we report the use of p-type semiconductor electrodes in order to utilize solar energy for photo-electrochemical NADH regeneration modeling the “light reactions” occurring in chloroplasts. All-solid electrodes with no organometallic mediators were employed, in order to perform the *in situ* NADH regeneration without enzymes deactivation. While bare semiconductors were shown to produce only enzymatically inactive dimers (NAD_2), modification of the surface by electro-deposition of a thin layer of Pt or Ru metal caused the formation of 1,4-NADH as the main product. In particular a Pt/p-GaAs photocathode, illuminated by pure visible light (> 600 nm), showed an increased efficiency in NAD^+ reduction at low overpotentials (-0.75V vs Ag/AgCl) when compared to metal electrodes (> 7 fold), with no dimer detection. The latter evidence suggested a reaction pathway with no $NAD^{\cdot}$ intermediate formation. This hypothesis was supported by electrochemical investigations on the reaction mechanism. This study represents the first example of NADH regeneration at an illuminated semiconductor electrode.

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Keywords: *Enzymatic CO2 reduction; NADH regeneration; photo-electrochemistry; p-type Gallium Arsenide;*

Symposium on CO2 chemistry – III

O-315

AEROBIC DEGRADATION OF TRICLOSAN IN ACTIVATED SLUDGE -METHYLATION AND OTHER PROCESSES

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Triclosan is an antimicrobial agent which is widely used in personal care products such as toothpaste, soaps, deodorants, cosmetics and skin care lotions as well as other consumer goods. It is released after use via sewer system into sewage treatment plants. It has been demonstrated, that the elimination of Triclosan is very effective in waste water treatment with removal rates > 90%. However, the elimination pathways and the role of adsorption and biodegradation have not been identified yet. Transformation products may be emitted and of future concern.

In this study we present data on the degradation and methylation of Triclosan in activated sludge systems. Degradation products are elucidated by means of GC-MS and HPLC-MS/MS. Degradation products include chlorinated phenols as well as methylated products. Kinetic data for the different steps and conditions are presented for selected reactions. A mass balance of Triclosan in dissolved and particulate phases is performed to estimate the fraction of sorption and biodegradation. Samples from the environment are compared to the technical processes.

Keywords: *Triclosan; activated sludge; degradation; waste water treatment;*

New trends in organometallic chemistry – IV

O-316

AMMONIA ACTIVATION PROCESSES LEADING TO NOVEL AMIDO AND IMIDO IRIDIUM AND RHODIUM COMPLEXES

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Amido-bridged polynuclear complexes [{M(μ_2-NH$_2$)(diolefine)}x] (M = Ir, Rh; diolefin = 1,5-cyclooctadiene (cod) or tetrafluorobenzobarrelene (tfbb)) can be prepared by treatment of the methoxo-bridged compounds [{M(μ-OMe)(diolefine)}$_2$] with gaseous ammonia in diethyl ether at atmospheric pressure.[1] The nuclearity of these unprecedented parent amido complexes depends on the olefin (trinuclear for tetrafluorobenzobarrelene and dinuclear for 1,5-cyclooctadiene). They are active catalysts in hydrogen transfer reactions from isopropanol to unsaturated substrates. The studies performed on the diiridium(I) complex [{Ir(μ_2-NH$_2$)(cod)}$_2$] evidences the dinuclear nature of the species involved and the participation of the two iridium centers in the catalytic hydrogen transfer reactions. Interestingly, under the absence of unsaturated substrates the concerted alcohol dehydrogenation process gives rise to the formation of unusual mixed amido/imido tetraiiridium and bis(imido) triiridium clusters.

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Keywords: *N ligands; Rhodium; Iridium; Cluster compounds; Homogeneous catalysis;*

New trends in organometallic chemistry – IV

O-317

SURPRISES FROM OLD FRIENDS: NITRON, THE ALDER CARBENE, AND RELATIVES

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The paradigm-shifting report of the first stable crystalline *N*-heterocyclic carbene (NHC) 1,3-di-1-adamantylimidazol-2-ylidene (IAd) by Arduengo in 1991 showed that singlet carbenes may be sufficiently stable for isolation. IAd is an iconic carbene, which triggered the tremendous development of NHCs and related diaminocarbenes from laboratory curiosities to powerful workhorses in synthesis and catalysis. Conveniently, a limited number of NHCs have become commercially available, with 1,3,4-triphenyl-1,2,4-triazol-5-ylidene (**1**) introduced by Enders being the earliest such example. Unfortunately, prices exceed several hundred US$ per gram. We found that the low-cost analytical reagent Nitron, a relative of **1** that has been commercially available for more than a century, exhibits a hitherto unrecognised reactivity which is not compatible with its conventional mesoionic Lewis structure **2**, but rather is expected for its NHC-type tautomer **2'** and closely resembles that of **1**. In fact, the properties of **1** and **2'** as ligands in coordination chemistry turn out to be very similar.[1] We have investigated several other mesoionic instant carbenes related to Nitron, which are easily accessible from readily available starting materials. Another iconic carbene is (iPr$_2$N)$_2$C, which was published by Alder in 1996 as the first acyclic diaminocarbene to be isolated and structurally characterised. The 'Alder carbene' is commonly known as the simplest stable diaminocarbene. However, its reactivity has been much underestimated. We found that (iPr$_2$N)$_2$C is suitable for small-molecule activation[2] and even undergoes a β-fragmentation in solution already at room temperature. This is in stark contrast to the previous claims of inertness. The β-fragmentation process which we uncovered very recently is not limited to the 'Alder carbene'.

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Keywords: *Carbenes; Nitrogen heterocycles; Carbene ligands; C-H activation; Carbonylation;*

New trends in organometallic chemistry – IV

O-318

ASYMMETRIC P-C CAGE COMPOUNDS AND THEIR TRANSITION METAL COMPLEX CHEMISTRY

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Becker's famous phosphaalkyne and its phosphaalkene precursor have opened the field of P-C cage chemistry. During the process of working out this chemistry more systematically, we became aware of the high diastereoselectivity of the cage forming reactions. In the case of pentaphosphadeltacyclene studied intensively in our group, two consecutive cycloaddition reactions led to one pair of enantiomeric P-C cages containing 7 stereogenic centers.[1] By introducing a chiral auxiliary we were able to obtain both enantiomers separately.[2] Further investigations revealed a rapid epimerization equilibrium on the secondary phosphane unit of the molecule.

Since we regard asymmetric P-C cages as compounds of interest as highly space filling ligands in stereoselective catalysis, we investigated the transition metal complex chemistry of pentaphosphadeltacyclene in more detail. After successful complexation of the transition metal fragments $M(CO)_5$ (M = Cr, Mo, W), the study was expanded to suitable redox-active metals like Ru(II) and Rh(I). Pentaphosphadeltacyclene complexes with $M(CO)_5$ were obtained as a mixture of four isomers, whereas the ruthenium complex consisted only of one isomer because of sterical reasons. In contrast to that, coordination with rhodium resulted in unique dinuclear complexes.

Pentaphosphadeltacyclene is also prone to rearrangement reactions. Two rearranged P-C cages *viz. iso*-pentaphosphadeltacyclene and pentaphosphahomocuneane could be synthesized selectively under basic conditions. CD spectroscopy showed that these cages are again formed under complete stereo control. The complex chemistry properties of these sterically even more demanding cages were tested with the transition metal fragments $M(CO)_5$.

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Keywords: *Cage compounds; Cycloaddition; Phosphane ligands; Rearrangement; Steric hindrance;*

New trends in organometallic chemistry – IV

O-319

LITHIUM CARBENOIDS -UNCOVERING NEW REACTIVITIES FOR LONG-KNOWN COMPOUNDS

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Since the pioneering work of Simmons and Smith carbenoids are frequently used reagents in organic syntheses, above all in cyclopropanation reactions.[1] However, giving their potential as carbene precursors it is surprising that there are only few examples of the application of carbenoids in the formation of transition metal carbene complexes. Furthermore, compared to carbenes – which have experienced dramatic research interest over the past two decades – carbenoids have almost been neglected despite their versatile reactivity as ambiphilic reagents. This ambiphilicity of free carbenes has opened a wide range of applications including their use in organocatalysis or in the stabilization of reactive species and the activation of small molecules such as dihydrogen or ammonia.[2]

Here we present the use of lithium/chloride carbenoids in the preparation of transition metal carbene complexes and bond activation reactions. Due to the high reactivity of carbenoids we focus on stabilized representatives, above all thiophosphinoyl substituted compounds. We show that depending on the stabilizing ability of a second functional group different reactivities are observed. As such, treatment of silyl substituted Li/Cl carbenoids with a palladium(0) precursor delivers either a thioketone complex – resulting from the reduction of the thiophosphinoyl moiety to the free phosphine – or a carbene complex.[3] Furthermore, these carbenoids show unexpected reactivities towards small molecules such as boranes, which clearly demonstrate their different reactivity compared to simple organolithium reagents and free carbenes.[4]

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Keywords: *carbene ligands; carbenoids; lithium; transition metals; carbanions;*

New trends in organometallic chemistry – IV

O-320

PALLADIUM(II) COMPLEXES WITH SMALL N-HETEROCYCLIC CARBENE LIGANDS AS HIGHLY ACTIVE CATALYSTS FOR THE SUZUKI-MIYAURA REACTION

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Palladium complexes, bearing bulky N-heterocyclic carbene ligands (NHC), found many applications in catalytic reactions and, in particular, in the Suzuki-Miyaura cross-coupling. In contrast, much less is known about reactivity of carbene palladium complexes bearing small substituents at N-atoms of imidazole ring. Consequently, we synthesized two groups of palladium(II) complexes, namely monomeric, of the type $Pd(NHC)_2X_2$ and dimeric of $[PdX_2(NHC)]_2$ composition with the aim to apply them in the Suzuki-Miyaura reaction. Moreover, mechanistic studies were undertaken in order to recognize structural transformations of palladium complexes under reaction conditions. All new complexes were characterized by spectroscopic and X-ray methods and, in particular, for $Pd(bmim\text{-}y)_2Br_2$, (bmim-y = 1--methyl-3-butylimidazol-2-ylidene) both isomers, *cis* and *trans*, were obtained. All of the complexes studied exhibited very high activity in Suzuki-Miyaura cross-coupling in ethylene glycol, achieving TONs of up to 760000. High activity was also noted when $NaBPh_4$ was used instead of $PhB(OH)_2$. ESI-MS studies of the reaction mixtures allowed to identify dimeric forms of the type $Pd_2(NHC)_4X_3^+$ and trimeric intermediates of the composition $Pd_3(NHC)_4Ph^+$, most probably participating in the catalytic cycle. Further studies, performed with TEM method, confirmed the presence of Pd(0) nanoparticles in the reaction mixture. Interestingly, the size of nanoparticles decreased during Suzuki-Miyaura reaction indicating on their solubilization with formation of soluble palladium species. Consequently, we proposed a homogeneous pathway of the reaction with the participation of palladium species bearing imidazolium cations or N-heterocyclic carbenes as key intermediates.

Keywords: *palladium; carbene ligands; cross-coupling; homogeneous catalysis; ligands effects;*

Young inorganic chemistry day – I

O-444

BASE-ASSISTED METAL-CATALYZED C-H BOND FUNCTIONALIZATIONS

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Direct C–H bond functionalizations of (hetero)arenes are highly attractive tools for an overall streamlining of synthetic chemistry, since these methods avoid the preparation and use of prefunctionalized starting materials.[1] Recently, we introduced carboxylates as efficient cocatalysts for site-selective direct arylations and alkylations employing inexpensive ruthenium complexes,[2] which were found to display complementary selectivities as compared to palladium(0)- or copper(I) catalysts.[3] Detailed mechanistic insight into the C–H bond ruthenation step set the stage for the development of ruthenium-catalyzed twofold C–H bond functionalizations, as well as step-economical oxidative annulations of alkynes.[4] These oxidative C–H bond functionalizations could be performed in an aerobic fashion under ambient air,[5] and provided step-economical access to various important bioactive heterocycles.[4]

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Keywords: *C-H activation; Ruthenium; Carboxylate ligands; Green chemistry; Homogeneous catalysis;*

Young inorganic chemistry day – I

O-445

NOBLE METALS – CONTAINING POLYOXOMETALATES

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Polyoxometalates (POMs)[1] containing noble metals, in particular palladium and platinum, have gained special attention over the last years.[2-4] Incorporation of noble metal ions in POM frameworks allows keeping the former soluble in aqueous or organic media and at the same time encapsulated in a fully inorganic, thermally and redox stable metal-oxo matrix. Such features offer a distinct advantage over noble metal coordination complexes displaying a set of organic ligands or organometallic moieties, susceptible to oxidative degradation.

Here we report on a novel series of Pd^{II} containing polyoxotungstates based on the monolacunary Keggin-type $[Pd_2(\alpha\text{-}XW_{11}O_{39})_2]^{n-}$ ($X=P^{V}$, $n=10$;[5] $X=Si^{IV}$, Ge^{IV}, $n=12$) and Dawson-type $[Pd_2(\alpha_2\text{-}P_2W_{17}O_{61})_2]^{16-}$ [5] polyanions comprising two POM ligands linked via two Pd^{II} centers in square-planar coordination environment. Several structural isomers vary by relative orientation of POM ligands have been isolated. The stability of the Pd^{II} containing POMs in both aqueous and organic solutions has been investigated using ^{31}P and ^{183}W NMR spectroscopy. The Pt^{II} analogue $[Pt_2(\alpha\text{-}PW_{11}O_{39})_2]^{10-}$ has also been prepared and characterized in the solid state and solution whereas reaction of $[\alpha\text{-}PW_{11}O_{39}]^{7-}$ with Pt^{IV} led to rather unexpected products.

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Keywords: *Polyoxometalates; Noble metals; Palladium; Platinum; NMR;*

Young inorganic chemistry day – I

O-446

POMZITES: A NEW CLASS OF MICROPOROUS INORGANIC FRAMEWORKS FROM A MINIMAL BUILDING BLOCK LIBRARY

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The crown-type heteropolyanion, $[P_8W_{48}O_{184}]^{40-}$ (hereafter referred to as $\{P_8W_{48}\}$) is notable for several properties including its high-negative charge, nanometer-sized cavity and remarkable electrochemistry.[1] Its inherent pore space means $\{P_8W_{48}\}$ is an ideal candidate as a network synthon, to prepare open framework materials with microporosity.[2] The preparation of such "POMzite" materials, and open frameworks with designed topologies in general, requires control of two main factors; statistics (molar ratios of the components) and geometry (transition metal coordination modes). Recently, such structures have been prepared by introducing first row transition metals to aqueous solutions of $\{P_8W_{48}\}$, however the desired control in preparing $\{P_8W_{48}\}$-based porous frameworks remains a challenge.

In the case of $\{P_8W_{48}\}$ assemblies, framework extension is highly dependent on experimental conditions such as pH, temperature and the presence of secondary cations. To understand this, and crucially to manipulate it in the formation of targeted networks, the binding properties of $\{P_8W_{48}\}$ were investigated revealing crown ether-like behaviour of the $\{P_8W_{48}\}$ ring.[3] Mapping the binding sites around the ring has enabled structural classification and comprehensive topological analysis, shedding light on a fascinating class of porous materials. Among many desirable properties, POMzite materials have shown remarkable single-crystal to single-crystal transformations, tunable and gateable guest uptake dependent on the redox state of the framework, and great potential as radioactive sequestrants.[2]

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Keywords: *Polyoxometalates; Supramolecular chemistry; Microporous materials;*

Young inorganic chemistry day – I

O-447

TOWARDS ROOM TEMPERATURE PHOTOMAGNETIC MOLECULAR SWITCHES: TRANSITION METAL COMPLEXES WITH PHOTOACTIVE LIGANDS

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Spin-crossover (SCO) and valence-tautomeric (VT) metal complexes are among the best known classes of molecular bistable systems. Their optical, magnetic and other physicochemical properties can be reversibly switched by changing the temperature, applied pressure, or irradiation with light. Although photoswitching in SCO complexes is well documented as a light-induced excited spin state trapping (LIESST) effect, this phenomenon is usually operative at low temperatures $T < 50$K. This imposes serious limitations for its application in genuine photodevices. The photoswitching in VT systems is even more difficult to achieve: temperatures below 20K are necessary to stabilize a photoinduced state.

We develop molecular coordination compounds that should overcome low-temperature limitations of the LIESST effect and would allow the photoswitching in SCO and VT systems at room temperature. To accomplish this we introduce *photoactive ligands* to metal ions in SCO and VT complexes in such a way that photoisomerization of the photoactive ligand modifies the ligand field. This light-driven modulation should induce a spin transition at the metal ion in SCO complexes or a photoinduced electron transfer in VT systems. Since the photoisomerization of the ligand can be easily accomplished at room temperature, the photoswitching of electronic states for both SCO and VT systems can be accomplished at room temperature as well.

We will report on the synthesis, characterization and investigation of photophysical properties of a series of photoactive ligands and their first-row transition metal complexes. *Diarylethene*-based ligands, capable of photocyclization/photocycloreversion in the solid state, are used to achieve a photoinduced spin transition in SCO complexes in solution and in the solid state. Whereas *cis-trans* photoisomerizable ligands are utilized to obtain a photoinduced electron transfer in VT complexes in solution.

Keywords: *Spin crossover; Valence isomerization; Magnetic peoperties; Molecular devices; Photochemistry;*

Young inorganic chemistry day – II

O-448

RUTHENIUM COMPLEXES HOPPING AT LIPID BILAYERS VIA A LIGHT-SENSITIVE SUPRAMOLECULAR BOND

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Our general interest lies in understanding coordination chemistry at lipid bilayers. Lipid bilayers represent well-defined surfaces, on which individual molecules may be moved by light. We have synthesized ruthenium complexes of the type [Ru(terpy)(N-N)(SRR')]2+, where N-N is a diimine chelate, and SRR' a thioether-cholesterol conjugate. Coordination of the sulfur atom to the metal complexes and insertion of the cholesterol moiety into the lipid bilayer allows for preparing Ru-decorated large unilamellar vesicles that were characterized by DLS, cryo-TEM, and UV-vis spectroscopy.[1] Upon visible light irradiation, the Ru-S coordination bond is selectively cleaved, releasing the aqua complex [Ru(terpy)(N-N)(OH2)]2+. When the bilayer is made of anionic lipids the "free" aqua Ru complex stays close to the membrane and coordinates back to the membrane-embedded thioether ligand, thus making a new Ru-S bond at the bilayer-water interface. With unhindered N-N chelates such coordination reaction only takes place upon heating, but with hindered N-N chelates it takes place at room temperature within tens of minutes.[2] In such case [Ru(terpy)(N-N)(SRR')]2+ and [Ru(terpy)(N-N)(OH2)]2+ are in thermal equilibrium, and the Ru-S bond appears as a light-sensitive supramolecular interaction. By repeatedly shining light on the vesicular system and leaving it in the dark we were able to cleave photochemically and attach thermally the Ru complex from and to the membrane, thus realizing light-controlled hopping of the metal complex at a lipid bilayer surface. We will discuss the influence of the charge of the lipids on the ruthenium-membrane interaction, and the possible application of such ruthenium-decorated vesicles for drug delivery purposes.

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Young inorganic chemistry day – II

O-449

STRUCTURAL CONTROL OF PHOTOINDUCED DYNAMICS IN 4H-IMIDAZOLE RUTHENIUM COMPLEXES

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Ruthenium-polypyridine complexes containing 4H-imidazole ligands constitute an interesting class of dyes, which are capable of absorbing light over a wide range of the visible spectrum.[1, 2] This renders these structures interesting for light-harvesting applications as, e.g., sensitizers in dye-sensitized solar cells.

Combining the results of resonance Raman and ultrafast transient absorption spectroscopy with TDDFT calculations, the photophysical properties of these systems were investigated in detail. The results indicate clear structure-dynamics relationships, relating excited-state properties to, e.g., the substitution pattern of the 4H-imidazole ligand and the polypyridine fragment. In terpyridyl-4H-imidazole complexes the introduction of electron--donating/electron-withdrawing substituents in the 4H-imidazole sphere allows to tune the relative energetic position of the excited states involved in the photoinduced dynamics and hence influence the path of intramolecular electron transfer. Surprisingly, upon exchanging the terpyridyl-complex fragment by a bipyridyl fragment, the decay is significantly accelerated. From these investigations conclusions will be drawn for the applicability of 4H-imidazole based Ruthenium dyes as, e.g., sensitizers in dye-sensitized solar cells.

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Keywords: *Ruthenium; Photophysics; time-resolved spectroscopy; ligand effects; substituent effects;*

Young inorganic chemistry day – II

O-450

CHROMOPHORE CONTAINING INORGANIC-ORGANIC HYBRID SILICA FOR PHOTONIC APPLICATIONS: DESIGN, SOL-GEL SYNTHESIS AND LUMINESCENCE PROPERTIES

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A variety of arene chromophores has been converted into sol-gel precursors for the synthesis of different kinds of micro- or mesoporous materials. Using both „classic' organic synthesis, e. g. *N*-alkylation or ester aminolysis as well as palladium catalyzed C-C and C-Si couplings, a large number arenes carrying one or more hydrolyzable siloxane groups has been made available. For a series of 5-(trimehoxysilyl-)thien-2-yl arenes, the detected fluorescences cover almost every part of the VIS spectrum. The fluorescence may as well be tuned by treating the organosilica with strong Lewis or Bronsted acids or *via* electrochemical processes, as it is the case with hybrid materials featuring covalently bound acridone or phenothiazine moieties.

Depending on the sol-gel method and the precursors used, meso- and microstructured hybrid materials have been obtained either *via* co-condensation or post-synthetic grafting. The morphology and structure of the silica range from monolithic xerogels to finely dispersed MCM-41 or SBA-15. Some of the materials incorporate high contents of organic chromophores of up to 24 weight-%. Colored or white light emitting glasses can be easiliy obtained by immobilization of very low dye contents inside a SiO_2 or organosilica framework.

Non-porous "Fluorogels", which could be produced in a one-pot sol-gel synthesis using the described chromophores, have proven to be more stable towards thermal stress than their microporous xerogel analogues. The compounds and materials we describe may therefore be suitable for a variety of photonic applications, including thin film silica coatings and membranes for sensors, polymeric optical fibres (POFs) and light emitting diodes (LEDs).

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Keywords: *Organic-inorganic hybrid composites; Sol-gel processes; Mesoporous materials; Microporous materials; Fluorescence;*

Young inorganic chemistry day – III

O-451

LIBRARIES OF MONODENTATE PHOSPHORUS LIGANDS FOR RHODIUM-CATALYZED ASYMMETRIC REACTIONS

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In the last decade, monodentate phosphorus ligands (e.g. phosphites, phosphonites, phosphoramidites and phosphinamines) have held the stage in asymmetric catalysis (Reetz, M. T. *Angew. Chem. Int. Ed.* **2008**, *47*, 2556-2588). The modular nature of all these ligands allows the synthesis of a wide variety of representatives, thereby making a combinatorial approach possible. An important breakthrough in this area was the use of binary mixtures of chiral monodentate P-ligands in several asymmetric rhodium catalyzed reactions: by mixing two ligands (L^a and L^b) in the presence of Rh, three species can be formed: RhL^aL^a, RhL^bL^b (homocomplexes), and RhL^aL^b (heterocomplex). The heterocombination is often more reactive and more (regio-, diastero- and enantio-) selective than either of the two homocombinations. The ideal case would constitute an equilibrium completely in favor of the heterocomplex [RhL^aL^b] because then only a single well-defined catalyst would exist in the reaction, and the undesired competition of the less selective homocomplexes would be avoided.

More recently, supramolecular approaches to the development of new ligands for asymmetric catalysis gained momentum (Carboni, S.; Gennari, C.; Pignataro, L.; Piarulli, U. *Dalton Trans.* **2011**, *40*, 4355-4373). The term ‘supramolecular ligand’ encompasses all the ligands possessing, besides the atom(s) coordinating the catalytic metal, an additional functionality capable of non-covalent interactions (mainly hydrogen or coordinative bonds) which can play the following role: (**i**) self-assemble two monodentate ligands to form a so-called ‘supramolecular bidentate ligand’; (**ii**) bind the substrate(s) in proximity to the catalytic metal center in analogy to metalloenzymes.

Here we present our approaches to the assembly of monodentate P-ligands and their application to several Rh-catalyzed asymmetric reactions.

Keywords: *Asymmetric catalysis; Hydrogenation; Supramolecular chemistry; Hydrogen bonds; Combinatorial Chemistry;*

Young inorganic chemistry day – III

O-452

NOVEL N,N'-DIARYLATED BIS(MESOIONIC CARBENE) AMIDO PINCER LIGANDS AND APPLICATIONS OF THEIR METAL COMPLEXES

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The tendency of carbenes to bind more strongly to metal-centres compared to nitrogen- or phosphorous-based ligands, and the robust nature of the corresponding complexes, render the search for new stable carbenes as highly desirable due to the wide number of potential applications.

Recently, the preparation of free triazolylidenes (mesoionic carbenes MICs) has been reported, exhibiting greater donor properties than those of NHCs.[1] In addition, MICs have also proven to be competent ligands for transition metal-catalysis.

Pincer-type ligands are widely known to form robust metal complexes, due to the chelating effect. This has been demonstrated by the isolation of reactive species, such as metal hydride complexes, and has contributed to their application in catalysis.[2] Attempts to prepare Ni(II) complexes of bis(NHC) amino pincer ligands from the free carbenes have been unsuccessful, and only possible via transmetallation.[3] Recently, an N-amido-N Ni hydride complex has been isolated but only at very low temperature.[4] Access to more stable Ni-H complexes should be possible using ligand scaffolds of carbene-amido--carbene type. However, few examples of such ligands exist, and none has been complexed to nickel.[2] Therefore, the synthesis of novel N,N'-diarylated 1*H*-1,2,3-triazol-5-ylidene amido pincer ligands, featuring either a rigid 3,6-di-*tert*-butyl-9*H*-carbazole or a more flexible and more donating dialkyl-amido backbone, will be presented as well as the corresponding nickel complexes.

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Keywords: *Ni(II) complexes; mesoionic carbenes; pincer ligands;*

Young inorganic chemistry day – III

O-453

MOLECULAR METAL-OXIDES AS VISIBLE-LIGHT DRIVEN SYNTHETIC OXYGEN EVOLVING CATALYSTS

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Over the last decades, the activation of small molecules such as H_2O has attracted increasing interest from a wide variety of fields of research, as the photochemical splitting of water into molecular oxygen and hydrogen can be used to convert solar energy into secondary energy carriers.

Water oxidation is the particularly challenging half-reaction and the development of highly stable and highly active water oxidation catalysts (WOCs) based on economically viable materials is at the forefront of chemical research.

In our work, we focus on the development of purely inorganic, metal-oxide-based systems, so-called polyoxometalates,[1] where 3d transition metals are incorporated as catalytic sites in a redox-active metal-oxide cluster shell. Conceptually, this incorporation can lead to the stabilization of catalytic metal centres in high oxidation states[2] which can subsequently be used as photoactive redox-centres for visible-light driven electron transfer reactions.[3]

Here, we show how this concept is employed to access a manganese vanadium oxide cluster, $\{Mn_4V_4\}$ as a synthetic mimic of the oxygen evolving complex (OEC) of Photosystem II. The $\{Mn_4V_4\}$ unit features a high-valent $[Mn_4O_4]^{6+}$ cubane which is stabilized by coordination to a tripodal vanadium oxide cluster, $[V_4O_{13}]^{6-}$. The compound can be used as a homogeneous oxygen evolving catalyst and it is shown that this water oxidation can be driven photochemically using $[Ru(bpy)_3]^{2+}$ as a visible-light photosensitizer. The compound shows turnover numbers of *ca.* 20 and shows high reversible redox-activity and solution stability. The deactivation mechanism under turnover conditions, deactivation products and possible stabilization routes are discussed.

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Keywords: *water splitting; Photochemistry; Energy conversion; Sustainable Chemistry; Catalysis;*

Young inorganic chemistry day – III

O-454

NUCLEOPHILIC ARYL-FLUORINATION AND ARYL-HALIDE EXCHANGE REACTIONS MEDIATED BY A CU(I)/CU(III) CATALYTIC CYCLE

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The insertion of a fluorine atom at an aryl group through halide exchange reactions is a highly desired transformation because of the importance of fluorinated pharmaceuticals and agrochemicals.[1] Moreover, the ability to exchange a given halide in an aryl group for another halide would facilitate the versatility of many transition metal catalyzed cross-coupling reactions, limited for many processes to the most reactive aryl iodide.[2, 3] Copper-catalyzed halide exchange reactions under very mild reaction conditions are described for the first time using a family of model aryl halide substrates.[4] All combinations of halide exchange (I, Br, Cl, F) are observed using catalytic amounts of copper(I) in the presence of excess of halide salt in moderate to high yields. Strikingly, quantitative fluorination of aryl halide substrates is also achieved catalytically at room temperature, using common fluoride sources, via the intermediacy of well-defined aryl-copper(III)-halide complexes.[4, 5] Experimental and computational data support a redox Cu(I)/Cu(III) catalytic cycle that involves aryl halide oxidative addition at the copper(I) center, followed by halide exchange and reductive elimination steps. Additionally, defluorination of the aryl fluoride model system can be also achieved with copper(I) at room temperature operating under a Cu(I)/Cu(III) redox pair.

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Keywords: *copper; cross-coupling; fluorides; homogeneous catalysis; hypervalent compounds;*

Young inorganic chemistry day – III

O-455

SYNTHESIS, STRUCTURE AND CATALYTIC PROPERTIES OF TRANSITION METAL COMPLEXES WITH SPACER-SEPARATED BIS-SILYLENE LIGANDS

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Silylenes, heavier analogues of carbenes, have attracted enormous research interest due to their interesting properties and reactivity. Despite the fact that isolable silylenes are no longer laboratory curiosities and can serve at the same time as much stronger σ-donor and π-acceptor ligands toward transition-metals than phosphine ligands,[1] bidentate bis-silylene ligands are unknown to date. In the present work, we have synthesized spacer-separated bis-silylenes **1,3** and **5** and their transition metal complexes **2,4** and **6**. Bis-silylene oxide LSiOSiL ($L7=7PhC(NtBu)_2$) **1** was prepared by dehydrochloration of the corresponding disiloxane with base. The reaction of **1** with $[Ni(COD)_2]$ leads to the first bis-silylene oxide nickel complex **2**.[2] Catalytic application of nickel complex**2** as a pre-catalyst for C-C coupling reactions will be presented. Furthermore, we will show the synthesis and isolation of the first Si(II)-based SiCSi pincer arene **3** and its unusual coordination behaviour towards palladium.[3] The electron-rich Lewis-donor character of Si(II) in pincer arene **3** gives facile access to new oligosilylene-silyl(phenyl) transition-metal complexes with potential application in catalytic chemical transformations. The successful synthesis, characterization and reactivity of the first bis(silylenyl)-substituted ferrocene LSiFcSiL **5** will be reported.[4] Compound **5** represents one of the strongest bidentate M(II)-based s-donor ligands as shown by coordination of **5** to [CpCo] to give the cobalt complex **6**. In addition, catalytic abilities of **6** for the Co-mediated [2+2+2] cycloaddition reactions of phenylacetylene and acetonitrile will be reported.

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Keywords: *Silicon; Transition metals; Main group elements; Carbene homologues; Si ligands;*

Biocatalysis Session – I

O-050

IN SILICO DISCOVERY AND APPLICATION OF TRANSAMINASES IN ORGANIC SYNTHESIS

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Transaminases are versatile enzymes for the synthesis of optically pure amines.[1] We have developed a protecting group strategy to broaden the substrate range, enhance reaction rates and enantioselectivity in w-transaminase-catalyzed kinetic resolutions.[2] To enable an efficient asymmetric synthesis to obtain the desired amine in high yield, the w-transaminase-catalyzed reaction was coupled with pyruvate decarboxylase.[3] This led to a considerable shift in the reaction equilibrium by formation of carbon dioxide and acetaldehyde. Furthermore, two high-throughput methods for the rapid determination of conversion and amino donor/acceptor spectrum were developed.[4, 5] Finally, a detailed *in silico* analysis algorithm was designed. This enabled the discovery of a toolbox of 17 (*R*)-selective transaminases[6] from >5,000 protein sequences of enzymes from the PLP-superfamily with predicted substrate type and enantiopreference. These new transaminases showed excellent activity and strict (*R*)-selectivity in the asymmetric synthesis of a broad set of chiral amines.[7]

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Keywords: *Biocatalysis; Enantioselectivity; Asymmetric synthesis;*

Biocatalysis Session – I

O-051

SYNTHETIC STUDIES TOWARDS DIHYPOESTOXIDE

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The synthetic studies have been described towards diterpene derived complex natural product dihypoestoxide via a hetero-Diels-Alder dimerisation of its proposed biosynthetic precursor, hypoestoxide. The tricyclic spirochroman core of dihypoestoxide has been synthesised from geranoic acid in seven steps using a hetero-Diels-Alder cycloaddition as a key step, thus providing support for the proposed biosynthesis of the natural product. Furthermore, analysis of the ^{13}C NMR data obtained for all four diastereoisomers of the synthetic spirochroman core has allowed us to propose a full stereochemical assignment for dihypoestoxide.[1] Our synthetic strategy towards hypoestoxide was based on a biomimetic approach by converting epiverticillol into its more oxygenated variant, hypoestoxide, A hetero-Diels-Alder dimerisation of hypoestoxide would then result into dihypoestoxide.

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Keywords: *Synthesis design; Synthetic methods; Natural products; biomimetic synthesis; biosynthesis;*

Biocatalysis Session – I

O-052

SOLUTION STRUCTURES AND MODELS DESCRIBING THE THIOREDOXIN SYSTEM FROM MYCOBACTERIUM TUBERCULOSIS

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Mycobacterium tuberculosis (*M. tb*) resists oxidative killing in part by using the thioredoxin (Trx) system.[1] Trx catalyzes thiol-disulfide exchange reactions using redox active cysteine thiols to reduce disulfides of other essential proteins, including metabolically essential enzymes.[2–4] Oxidized Trx is then reduced by thioredoxin reductase (TrxR) in an NADPH dependant reaction.[5] The *M. tb* Trx system consists of three Trx's (TrxA, TrxB, and TrxC) and one Trx reductase (TrxR). TrxR is essential for survival. TrxB and TrxC are known substrates of TrxR.[1] TrxA, meanwhile, has been reported to not bind to TrxR and to possibly be "cryptic".[1] The *M. tb* Trx system is dissimilar to the human Trx system (25–35% indentity) such that inhibitor specificity for the *M. tb* Trx system should be obtainable. Thus, the *M. tb* Trx system appears to be a viable drug target.[6]

The objective of this study was to structurally characterize oxidized and reduced Trx's. Solution structures have been calculated using standard NMR solution experiments.[7] Our studies indicate that TrxA is well-folded in both oxidized and reduced states. Structures of the individual Trx's and binding models of the TrxN(N = A, B, or C)-TrxR, constructed from NMR titrations of each ^{15}N enriched TrxN and unlabeled TrxR, are discussed.[7] These binding models show an empty pocket between the Trx and the TrxR, that is targeted for structure-based design of uncompetitive inhibitors.

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Keywords: *Mycobacterium tuberculosis; nuclear magnetic resonance; structural biology; thioredoxin system;*

Biocatalysis Session – I

O-053

THE LIGHT MAKES IT WORKS. MOLECULAR REACTION DYNAMICS INVESTIGATION AT ULTRAFAST TIME SCALE ON NADPH:PROTOCHLOROPHYLLIDE OXIDOREDUCTASE

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The light driven NADPH:protochlorophyllide oxidoreductase (POR) is a key enzyme of chlorophyll biosynthesis in angiosperm and cyanobacteria. POR's unique requirement of light to became active, makes the enzyme an attractive model to study the dynamics of enzymatic reaction in real time. It catalyzes one of the later steps in the chlorophyll synthesis pathway: the light-dependent reduction of protochlorophyllide (PChlide) to chlorophyllide by *trans* addition of hydrogen across the C17-C18 double bond in the porphyrin ring.

The ternary complex NADPH-POR-PChlide has been reconstituted in vitro and the initial reaction steps were followed using various spectroscopic tools such as femtosecond/picosecond time-resolved absorption and fluorescence spectroscopy in the UV/vis spectral range. To highlight the mechanistic interplay between the protein moiety and enzyme function, point mutations were introduced into the catalytic site.

Two point mutants, have been produced: an aspartate was substituted by methionine and a serine by alanine. Here we report our first results on three POR isoforms: POR A and POR B from barley (*Hordeum vulgare*) and POR from *Synechocystis*. We observed that the fluorescence decay time of PChlide when bound to the protein WT (wildtype) is about 1 ns longer than in solution. We compared the kinetic parameters of the photoreaction with the fluorescence decay time for the different isoforms and mutants. We also discuss the role of these substitutions in the substrate binding site and their effect on the H-bond network, which we suggest to play a prominent role in first fast reaction steps.

Keywords: *Enzyme models; Mutagenesis; Time-resolved spectroscopy; Oxidoreductases;*

Biocatalysis Session – II

O-054

BIOCATALYTIC CARBOXYLATION

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The use of CO_2 as raw material for the synthesis of well-defined organic compounds has been rapidly developed over the last couple of years.[1] The Kolbe-Schmitt reaction,[2] which is one of the major protocols for the production of aromatic carboxylic acids on industrial scale, requires harsh reaction conditions (high pressure and temperature). In contrast, a biocatalytic method based on decarboxylases catalysing the reverse (carboxylation) reaction represents a promising 'green' alternative for the regioselective carboxylation of aromatics.

In order to evaluate the potential of this novel strategy, several benzoic and phenolic acid decarboxylases were applied to a range of aromatic substrates, using bicarbonate buffer as CO_2-source. Whereas benzoic acid decarboxylases catalysed the selective *o*-carboxylation of phenolic substrates yielding the corresponding *o*-hydroxybenzoic acids, such as salicylic acid, phenolic acid decarboxylases enabled the side-chain carboxylation of hydroxystyrene derivatives at C_{beta}.[3] For the latter transformation, no chemical counterpart exists.

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Keywords: *Carboxylation; carboxylic acids; Biotransformations; Biocatalysis;*

Biocatalysis Session – II

O-055

PEPTIDE ADSORPTION ON ZRO_2, TIZR AND TIO_2 SURFACES

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Interactions between peptides and inorganic materials are in the focus of different research fields like nanotechnology or biotechnology as peptides offer new possibilities for surface modifications. Utilizing specific surface binding peptides as anchor allows adapting various properties such as corrosion behavior and surface hydrophobicity or developing sensor surfaces. Another important application consists in the development of biocompatible implant materials. Biofunctionalization of materials can be achieved by the conjugation of surface binding peptides with biologically active proteins for the oriented immobilization.

This work investigated on the peptide adsorption on different implant materials. The ceramics zirconium oxide (ZrO_2), the metal alloy titanium zircon (TiZr) and the metal titanium (c.p.Ti) were examined in regard to the peptide adsorption, the kind of interactions and the influences of ion concentration, pH value and temperature.

Eight different peptides were selected from literature. Three have already been proven to adsorb to TiO_2 and TiZr and two peptides were chosen for adsorption testing on ZrO_2 surfaces. The presence of immobilized peptides was confirmed and quantified by the following surface analysis methods: an enzymatic assay based on biotin-streptavidin interactions, surface plasmon resonance (SPR) and fluorescence measurements.

Three of the eight examined peptide sequences showed stable binding to all investigated materials. The surface densities of immobilized peptides on $ZrO_{2,}$ TiZr and TiO_2 range from 20 to 50 pmol/cm². The comparison of the surface densities gained by enzymatic assay and the SPR measurements showed equivalent results.

Herein, promising linker molecules for a modification of the typical implant materials ZrO_2, TiZr and Ti were identified. They showed stable adsorption even under physiological conditions which enables them for biofunctionalization of implants to improve their biocompatibility.

Keywords: *Adsorption; Immobilization; Materials science; Medicinal chemistry; Peptides;*

Biocatalysis Session – II

O-056

MICHAEL ADDITION OF WATER: AN ENZYMATIC ENANTIOSELECTIVE APPROACH

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The addition of water to carbon-carbon double bonds at first glance seems straightforward. However, both chemically and enzymatically this reaction is very difficult to perform. Indeed the Michael addition of water is virtually unknown.[1] However, recently a Michael hydrates was identified. Interestingly, the hydration product is further oxidized to a 1,3-diketone by the same enzyme which was therefore named Michael hydratase ÷ alcohol dehydrogenase MhyADH.[2] Fascinatingly, this bifunctional enzyme can also be used to catalyze only one of the two steps. The hydroxylation of alpha beta unsaturated ketones can be uncoupled because in the absence of electron acceptors MhyADH functions only as a hydratase, considerably extending the scope of the enzyme. To efficiently work with MhyADH, it was purified from *A. denitrificans* and the gene was cloned. The sequence of MhyADH revealed that this enzyme belongs to the molybdenum-containing hydroxylases which contain two Fe_2-S_2 clusters, one FAD and two molybdopterins which coordinate a molybdate.[3] We will report on the purification, characterization and application of MhyADH. The focus will be on the enantioselective addition of water to the unsaturated conjugated carbonyl compounds. Enantioselectivity and substrate scope of the enzyme will be discussed and first mechanistic studies will be presented. Another problem of this reaction, the position of the equilibrium, will be addressed. Although one might assume that the reaction will always give quantitative yields since the reaction is performed in water and a powerful driving force is therefore present, this is not the case.

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Keywords: *Michael Addition; enzyme catalysis; Enantioselectivity; Metalloenzymes;*

Biocatalysis Session – III

O-057

THE QUEST FOR MILD AND EFFICIENT OXIDATIVE AGENTS: SYNTHETIC EXPLOITATION OF LACCASES

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Laccases are oxidoreductases belonging to the multinuclear copper-containing oxidases. The overall outcome of their catalytic cycle is the reduction of one molecule of oxygen to two molecules of water and the concomitant oxidation of four substrate molecules to give four radicals.[1, 2]

Typical substrates of laccases are phenols and aliphatic or aromatic amines, the reaction products being mixtures of dimers or oligomers derived by the coupling of the reactive radical intermediates. For instance, we have exploited these biotransformations to isolate new dimeric derivatives of natural phenolic derivatives (resveratrol and its analogues, β-estradiol, totarol, sylibin). In these studies we have also observed a significant influence of the solvent on the reaction outcomes.

More recently, we have described the use of laccase-catalyzed reactions for the selective hydroxylation of ergot alkaloids and for the synthesis of the bisindole alkaloid anhydrovinblastine.

Additionally, laccases oxidation of non-phenolic groups, particularly benzyl and – more generally – primary alcohols, is also possible thanks to the ancillary action of the so-called “mediators” (i.e., TEMPO, HBT, ABTS): the oxidation step is performed by the oxidized form of a suitable mediator, generated by its interaction with the laccase. Accordingly, we have oxidized a series of sugar derivatives and of natural glycosides.

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Keywords: *biocatalysis; oxidoreductases; oxidation; natural products;*

Biocatalysis Session – III

O-058

QUANTITATIVE COMPARISON OF CHIRAL CATALYSTS' SELECTIVITY AND PERFORMANCE:A GENERIC CONCEPT ILLUSTRATED WITH CYCLODODECANONE MONOOXYGENASEAS BAEYER-VILLIGER BIOCATALYST

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This work establishes a generic tool for chiral catalyst evaluation based on the application-oriented properties activity and selectivity, aiming at the prospect to quantitatively compare catalysts' general performance on a multitude of substrates. It is designed and intended to serve as decision guidance for challenges in catalysis and comprehensible information extraction from already recorded but unrefined data sets. The underlying algorithm assigns function points to catalytic entities via a statistically solid model possessing high flexibility and thus generates a relative ranking. This is coupled to an automated iterative refinement process towards maximum information content in the results employing Shannon Entropy optimization. Consequently, the developed work-flow facilitates high distinguishability between catalysts even in low-scattering data sets. Complementing this, a clearly arranged graphic representation permits ready and reliable visual interpretation of generality or niche capabilities of catalysts. Usefulness of the title concept is demonstrated with the performance evaluation of cyclododecanone monooxygenase, a highly versatile Baeyer-Villiger enzyme. To retain broad applicability, an open-source MATLAB® script is made available in electronic form.

Keywords: *Biocatalysis; Asymmetric synthesis; Asymmetric catalysis;*

Biocatalysis Session – III

O-059

FROM RINGS AND CHAINS – SYNTHESIS OF HIGH VALUE COMPOUNDS VIA MONOOXYGENASE-CATALYSED REACTIONS

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Chemo-, regio- and enantioselective oxyfunctionalisation of carbon-hydrogen bonds is a hot topic in organic chemistry enabling scientists to streamline synthetic routes.[1] Therefore, monooxygenases as the nature's key to these transformations bear high potential for organic chemistry due to their ability to catalyse the selective insertion of an oxygen atom from atmospheric dioxygen into carbon-hydrogen bonds of a variety of organic compounds.[2] In the current project the P450 BM3 monooxygenase from *Bacillus megaterium* was chosen as an excellent platform for biocatalysis. It is a well characterised, highly active and self-sufficient enzyme[3] which was frequently turned into a powerful biocatalyst with desired properties concerning substrate spectra and hydroxylation patterns in engineering approaches.[4] The design of a versatile mutant library for the biocatalyst in combination with the application of state-of-the-art assays enables to search for variants that allow the selective functionalisation of sterically varying compounds in preparative scale. The respective products are required as key intermediates in the synthesis of (natural) active compounds. We will present our most recent efforts towards the chemoselective generation of benzylic alcohols and enantioselective formation of allylic alcohols *via* monooxygenase mutants.

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Keywords: *Biocatalysis; Oxidation; Alcohols;*

Biocatalysis Session – III

O-060

KNOWLEDGE-BASED (RE)DESIGN OF FLAVIN-CONTAINING BIOCATALYSTS

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The catalytic potential of enzymes is more and more appreciated by the industry and many industrial processes already rely on these sophisticated biocatalysts. However, the number of reactions catalyzed by enzymes is restricted as enzymes only have evolved to catalyze reactions that are physiologically relevant. Furthermore, enzymes have adapted to the cellular environment in which they have to function. This excludes the existence of enzymes that do not fit within the boundaries set by nature. It is a great challenge to go beyond these natural boundaries and develop methodologies to design ‘unnatural’ tailor-made enzymes. Ideally it should become possible to (re)design enzymes to convert pre-defined substrates. Such designer enzymes could theoretically exhibit unsurpassed catalytic properties and, obviously, will be of significant interest for industrial biotechnology.

Recent work in my research group has focused on discovery of new oxidative enzymes and using them as template for enzyme redesign studies. Examples of newly discovered and redesigned redox enzymes, flavoprotein oxidases and Baeyer-Villiger monooxygenases, will be presented. Mechanistic studies on these biocatalysts have revealed new insights in how these enzymes function. Using this knowledge, it has been possible to create artificial enzymes that display catalytic properties not observed in nature. Results on some recent enzyme redesign studies will be highlighted in which new artificial enzymes were created by cofactor redesign.

Keywords: *Biocatalysis; Enzyme catalysis; Oxygenation; Oxidation;*

Life Science Multisymposium – I

O-187

CHEMICAL BIOLOGY THAT CONTROLS DNA STRUCTURE AND FUNCTION

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Fifty years after the discovery of the double-helical structure of DNA, the complete sequence of the human genome has been determined. Many diseases, including cancer, hereditary, and viral diseases, can now be understood at the DNA sequence level. Recently, it has been revealed that epigenetic modification plays an important role in gene expression, which controls the gene expression through DNA methylation and histone modification. This is closely related to the cell reprogramming and differentiation. We have been undertaking original research on the molecular recognition of DNA by antitumor antibiotics, and the analysis of atom-specific chemical reaction toward DNA with these agents. By reconstituting such knowledge, various functionalized sequence-specific DNA binders were synthesized as an artificial genetic switch.[1] Furthermore we have demonstrated to control the reactions with DNA methylase and repair enzymes in a designed DNA nanostructure, DNA origami, and analyzed the single reaction using high-speed atomic force microscope (AFM).[2] Recent progress of regulation of the epigenetic gene expression using designed molecules, and elucidation the mechanism using single molecular imaging technique will be discussed.

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Keywords:

Life Science Multisymposium – I

O-188

NEW BISPIDINE-DERIVATIVE FOR DUAL-MODALITY IMAGING

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The diagnostic evaluation and treatment of complex diseases, like cancer, is very difficult using only standing alone methods with their individual limitations. To overcome these restrictions, a combination of different imaging modalities will be conceivable. The radionuclide based positron emission tomography (PET) and single photon emission computed tomography (SPECT) are useful for functional imaging. To obtain anatomical information, computer tomography (CT) and magnetic resonance imaging (MRI) can be used, whereas fluorescence-based optical imaging finds application in surgery guidance.[1]

Extensive research effort has shown, that 3,7-diazabicyclo[3.3.1]nonane-derivatives (bispidines) built up thermodynamic and kinetic very stable complexes with copper(II) ions (logK = 16.28).[2] Different functional groups of the backbone (hydroxyl and carboxyl groups) provide the opportunity for simultaneous attachment of dyes and biomolecules (e. g. peptides, proteins, antibodies) as vector molecules. After that functionalization, the complexation of radioactive copper isotopes (61Cu, 64Cu, 67Cu) allows visualization of cancer tissue with PET and radiotherapy.

The hydroxyl group at C9 was functionalized using nitrophenyl chloroformate for active ester generation. Therefore, a fluorescence label could be coupled to the bispidine by urethane bond formation.

We will report about the versatility of bispidines as compounds to realize different functionalities in one molecule. The synthesis and characterization of such derivative, and radiolabeling experiments with the PET-radionuclide 64Cu will be discussed.

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Keywords: *copper; radiopharmaceuticals; imaging agents;*

Life Science Multisymposium – I

O-189

MULTIFUNCTIONAL PEPTIDE NUCLEIC ACIDS (PNA) FOR MICRORNA TARGETING

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Peptide nucleic acids (PNA), and their modification are extensively used for targeting mRNA in the antisense approach for the down-regulation of the expression of target genes.[1] Micro-RNA (miR) are regulatory short (19–23 bp) dsRNA which modulate gene expression of highly relevant biological functions such as differentiation, cell cycle and apoptosis, through mRNA degradation. Inhibition of miR activity by specific molecules (anti-miR,) has been shown to be of great interest in drug development.[2]

In the present communication we describe the synthesis of anti-miR PNA either conjugated with a carrier peptide or bearing modified residues along the chain, PNA of high affinity and high specificity for miR210 and miR 221, involved in erythroid differentiation and tumor progression respectively were obtained. Modified PNA showed improved biovailability and effectively entered into tumor cells and exerted anti-miR acivity,[3] leading to up-regulation of genes. Backbone modified PNAs, bearing arginine side chains either at C2 or C5 carbon atom of the PNA backbone showed improved cellular uptake, and higher biostability than the peptide-conjugated, and effectiveness of these compounds was shown to depend on the type of substitution; and on the distribution of charges within the PNA strand.[4]

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Keywords: *Peptide Nucleic Acid; Modified Backbone; Anti-miR;*

Life Science Multisymposium – I

O-190

SINGLE VERSUS DOUBLE LAYER FIBRILLAR AMYLOID-BETA OLIGOMERS: SIZE DOES MATTER

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Alzheimer's disease (AD), the most common form of dementia world-wide, belongs to the class of protein misfolding diseases. The associated molecule is the 39 to 42-residues long amyloid-β peptide, that aggregates into oligomers, filaments, and fibrils found in plaque deposits in the brain of AD patients.

Notwithstanding the large efforts of the past decades, a viable cure for this disease is still not available. One reason for this is Aβ's conformational flexibility and structural heterogeneity in solution paired with its aggregation tendency. This renders the determination and isolation of distinct Aβ structures experimentally challenging. Especially the soluble oligomers, that are nowadays thought to be the causative agents in AD, may adopt a plethora of conformations in vivo.

In this context, we used molecular dynamics simulations to investigate the structural stability of fibrillar single and double layer Aβ42 oligomers of different size (4-mer to 48-mer), because it is known from experiment, that Aβ fibrils can be dissolved into toxic oligomers.

We found that there is a clear correlation between oligomer size and preference for double layer structure: Large oligomers display an enhanced stability in double layer conformation, whereas small oligomers prefer the single layer structure. On the other hand, large single layer oligomers disrupt into smaller oligomers, while small double layer oligomers collapse or are energetically unfavorable. From our simulations, we deduce that the critical number of oligomers to construct a stable Aβ double layer is in the range of 10 to 12.

In a more general picture, longitudinal growth along a single layer is limited by the increasing structural instability. Lateral growth, i.e. forming a double layer, creates stable mini-fibrils. These may act as seeds for further stable fibril growth. Our findings are important for the de-novo design of potential drugs targeting Aβ aggregation.

Keywords: *Molecular dynamics; Amyloid beta-peptides; Conformation analysis;*

Life Science Multisymposium – II

O-191

NANOMATERIAL AND PROTEIN ENGINEERING FOR MODULATING IMMUNE RESPONSES

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Biomaterials research has advanced to a state where materials are desined to possess specific biological, drug-like activity. Here, we will present work on materials and protein engienering approaches for applications in immunotherapeutics. Nanomaterials present intersting opportunities in the context of vaccination. Very small particles, in the sub-100 nm range, can traffic by interstitial flow to into the draining lymphatics and thus efficiently access dendritic cells resident there. Trafficking across mucosal surfaces can be efficient as well. We hae developed approaches by which to conjugate antigen and adjuvant molecules in a manner that leads to particularly efficient antigen cross-presentation and inducation of cellular immune responses, of relevance in vaccination versus infectious diseases and cancer.

We are also interested in approaches by which to prevent or erase immune responses, exploiting the body's mechanisms for maintenance of peripheral tolerance. Antigen collected from apoptotic cells is presented in a manner such that peripheral tolerance is induced or maintained to those antigens. We are exploring protein engineering approaches that might harness this mechanism, engineering peptide and protein antigens to bind to the surfaces of circulating erythrocytes, wich are cleared and processed as they age. We have observed that this leads to antigen-specific deletion of both CD4+ and CD8+ T cells. We will show potential applicability of this approach in both preventing immunity to protein drugs and in blunting autoimmune-induced pathology.

Keywords: *Biomaterial; Nanoparticle;*

Life Science Multisymposium – II

O-192

SYNTHESIS, PROPERTIES, AND APPLICATIONS OF COVALENTLY TETHERED MINICOLLAGENS

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C-terminal capping of three collagen peptides yields synthetic minicollagens of scalable lengths and melting temperatures. The covalently tethered triple helix is a non-bendable rod whose thermodynamic stability significantly differs from a monomeric PUG strand. Minicollagens adopt triple helical conformations independent of pH and buffers and therefore can serve as building blocks for molecular bionic designs. Their spectroscopic properties and an example of a possible application in material science are presented here.[1, 2]

Chiral triamines can fit the required stagger of the triple helix. These capping groups contribute to triple helix stabilization by ensuring an in-phase start of the triple helix. The cap optimized in length and chirality is improving the melting temperature by more than 20 °C. In this presentation we show that trimeric architectures of minicollagens up to sizes of almost 90 amino acids can be synthesized within one day in good qualities.[3]

Higher melting temperatures increase the range for minicollagens of certain lengths to exhibit a sigmoid melting behaviour. Physicochemical analyses also state a fast folding of those collagen derivatives. Contrasting previously synthesized collagens, the molecules presented here exhibit triple helical folding without incubation times. This opens new application fields for the minicollagens. One example from Material Science will be presented.[4]

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Keywords: *Peptides; Collagen; Sold-Phase Peptide-Synthesis;*

Life Science Multisymposium – II

O-193

DNA RECOGNITION: NEW SPECIFIC AGENTS AND FLUORESCENT PROBES

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Deciphering the human genome has opened new perspectives in biomedical research, promising improved diagnostic techniques and personalized therapies. However, to fully exploit the knowledge about our genes, it is necessary to develop probes capable of targeting and sensing specific DNA sequences. In the recent decades there have been significant contributions in the area of dsDNA recognition. However, despite the enormous developments in this area, specific targeting of particular DNA sequences still remains an unsolved problem in chemical biology.

In this context, during the last decade our group has reported some successful discoveries in the design, synthesis and study of non-natural peptide derivatives, which despite being structurally simpler, are capable of mimicking the DNA binding properties of the transcription factors.[1] Here, we present our steps forward in this field.

a) Development of specific DNA recognition by synthetic, monomeric Cys_2His_2 Zinc finger peptide conjugated to a minor groove binder.[2]

b) Discovery of the fluorogenic properties of the DNA minor groove binder BAPPA and applications.[3]

c) Straightforward access to bisbenzamidine DNA binders and use as versatile adaptors for DNA-promoted process.[4]

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Keywords: *Molecular recognition; DNA; Fluorescence; Peptides; Transcription factors;*

Life Science Multisymposium – III

O-194

OLIGONUCLEOTIDES FOR SPLICE-SWITCHING AND STRAND-INVASION

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Synthetic nucleic acid chemistry has made possible the generation of oligonucleotides (ONs) with special features allowing potent effects in biological systems. We have recently developed highly efficient ONs for the correction of pseudo-exon inclusions secondary to mutations in the BTK gene causing recessive, X-linked agammaglobulinemia (XLA). In XLA there is a differentiation block in the B-lymphocyte lineage resulting the absence of B-lymphocytes and plasma cell in affected individuals. Bacterial artificial chromosome (BAC) transgenic mice carrying the mutated human BTK gene were generated as a new model for the study of splice-switching. Following algorithm-based identification of suitable target sequences efficient correction of both mRNA and protein was observed using locked nucleic acid (LNA) as well as morpholino-based ONs in both reporter cell assays and in primary cells from both patients and BAC-transgenic mice.

We have also developed methods for strand-invasion into duplex DNA. The original “Zorro-LNA” construct is formed by two ONs, each targeting one of the two strands in a DNA duplex, and tethered by a hybridizing linker sequence. We have also studied single-stranded Zorro-LNAs devoid of any hybridizing region, but instead equipped with a single linker of different chemistry. Both of these compounds strand-invade DNA as evidenced by S1 nuclease assays. We have recently investigated the effect of Zorro-LNA on the expression of Huntingtin (HTT) mRNA in transfected cells. The HTT gene is mutated in patients with the dominantly inherited, neurodegenerative disorder named Huntington’s disease. By scanning the HTT gene, six different regions were identified and tested. Two of them showed robust down-regulation of HTT transcripts, when targeted by Zorro-LNAs. Reduced expression was also obtained in cell-lines from patients with Huntington’s disease.

Keywords: *DNA; Oligonucleotides;*

Life Science Multisymposium – III

O-195

INK-JET PRINTING FOR DRUG SCREENING BY DROPLET MICROARRAYS

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Drug screening is the complex process of retrieving chemical compounds able to modulate the activity of biological targets which are of interest for a disease. Conventional miniaturized drug screening technologies require time and reagent consuming (micro-, nanoliter scale) instrumental tools, liquid handling robotics and complex detectors. Here we show a low-cost and efficient drug screening methodology based on inkjet printing for delivering molecular systems in picoliter volumes coupled with easily-implemented detection tools for probing target-drug interaction. We firstly show up a screening platform for a model enzyme/substrate couple and we extend this approach to systems of clear interest for medicinal chemistry.

The approach was initially proved with a model enzyme system like Glucose Oxidase substrate covalently linked to a functionalized silicon oxide support.[1] On this support an enzymatic substrate (D-glucose)/inhibitor (D-glucal) couple was dispensed. A simple colorimetric detection method based on the production of a red quinoneimine dye in a reaction catalyzed by Horseradish Peroxidase proved the screening capability of the microarray at the single spot. Occurrence of competitive inhibition was verified at the solid-liquid interface with a similar behavior occurring for such system in a solution phase.[2]

Afterwards, this methodology has been extended to other systems including CYP450 enzymes like CYP3A4, one of the main targets for the phase I drug metabolism via a droplet microreactors arrays containing CYP3A4 enzyme mixed with model inhibitors (i.e. ketoconazole and erythromycin) and enzymatic chemiluminescent substrates (Luciferin-Isopropylacetate). Enzymatic activity in picoliter liquid spots was detected by using a low cost optical method. Accordingly, bioluminescence given by D-luciferin leads to a production of photons that increase spot brightness which can be quantified by Charge-coupled device camera.

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Keywords: *drug screening; inkjet printing; enzymes; microarrays; biotechnology;*

Life Science Multisymposium – III

O-196

DESIGN AND SYNTHESIS OF NOVEL G-QUADRUPLEX DNA STABILIZING MOLECULES

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G-Quadruplex DNA structures have gained enormous attention in recent years, due to their implication in critical biological processes, most notably cancer cell “immortalization” by means of telomere elongation by the enzyme telomerase, and the regulation of transcription of key proto-oncogenes (e.g. c-myc, c-kit). Both processes are linked to tumor formation, which has prompted efforts in the direction of development of small molecules with the ability to stabilize or induce G-quadruplexes in the G-rich DNA sequences of the human telomere or oncogene promoter regions. Stabilization of a G-quadruplex in these regions prevents recognition of the affected sequences by telomerase or the transcriptional machinery respectively, which results in arresting telomere elongation or oncogene expression, thus providing new promising anti-cancer mechanisms. As part of a broader effort to develop new classes of anti-cancer therapeutic agents and chemical probes for investigating yet unknown aspects of cancer biology pertaining to G-quadruplexes, we have designed and synthesized both organic and organometallic platinum-based compounds, as well as their conjugates with peptide nucleic acids (PNAs). Our design and synthetic methods for the preparation of these compounds, intended to be evaluated for their ability to induce or stabilize the G-quadruplex structure in biologically-relevant G-rich DNA sequences, will be described.

Keywords: *antitumor agents; cancer; G-quadruplexes; solid-phase synthesis; platinum;*

Life Science Multisymposium – III

O-197

DNA DAMAGE CHEMISTRY IN NUCLEOSOME CORE PARTICLES

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At one time the histone proteins were believed only to provide structural support for nuclear DNA. It is now understood that histone post-translational modification within nucleosomes plays a large role in gene regulation. The nucleosome is also increasingly recognized to affect other biochemical processes, including the rate at which DNA lesions are repaired. Due to the instability of some DNA lesions, such as abasic sites, decreased repair efficiency poses other problems such as increased amounts of strand scission. We have asked whether the histone proteins, which contain a large number of basic amino acids, actively participates in DNA damage chemistry? By taking advantage of methods that enable one to reconstitute nucleosomes containing DNA lesions at defined sites, we have shown that the histone proteins in nucleosome core particles catalyze DNA strand scission at abasic sites. The details of this chemistry and implications will be discussed.

Keywords: *DNA damage; nucleosomes; mechanism;*

Medicinal Chemistry session – I

O-321

STEREOSELECTIVE ACCESS TO NEW SCAFFOLDS BY PHOTOCHEMICAL REACTIONS

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Among all light-driven reactions, the [2+2] photocycloaddition is the synthetically most useful transformation.[1] In this lecture, most recent developments in the field will be discussed.[2] Particular emphasis is given on all aspects of stereoselectivity and on applications to the synthesis of new scaffolds. The quest for enantioselective [2+2] photocycloaddition reactions employing appro-priate chiral photocatalysts presents a formidable challenge for the pro-duction of biologically relevant compounds. Chiral catalysts for this endeavour have been developed in our laboratories and will also be presented in the course of the lecture.[3, 4]

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Keywords: *cycloaddition; enantioselectivity; medicinal chemistry; photochemistry; strained molecules;*

Medicinal Chemistry session – I

O-322

CONCISE ROUTES FOR EXPANDING THE DIVERSITY OF SELECTIVE CYCLOPEPTIDES HISTONE DEACETYLASE INHIBITORS

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Recently, we identified the natural product cyclopeptide FR235222, as a highly potent histone deacetylase inhibitor (HDACi), efficient at 8 nM on *Toxoplasma gondii*, the apicomplexa parasite responsible for toxoplasmosis, albeit with a poor selectivity index (efficiency against the parasite compared to cytotoxicity on human cell) with SI = 12.[1] We demonstrated that the inhibition of histone deacetylase HDAC3 with this HDACi induced epigenetic modifications, which strongly affected strain virulence at the tachyzoite and bradyzoite stages of the parasitic life cycle.[1, 2] This dual efficiency with a bioactive molecule on two distinct stages of the parasitic life cycle is unprecedented and outlines the key role of targeting the epigenetic mechanisms to control parasite proliferation.

The design of easy adjustable/customisable syntheses and according to the Diversity Oriented Synthesis principles (variations on appendages and skeletal diversities) is essential to reduce the time in the optimizing process by a direct access to structurally diverse and relevant bioactive products. We present in this communication our new synthetic strategy involving post-transformation reactions (appendage and skeletal modulations) on a common cyclopeptide scaffold that affords new bioactive HDACi in only one or two steps. These new structures combine structural features ranging from FR235222 to largazole and have shed light on important structure-activity relationships. As a result, we managed to optimize new synthetic cyclopeptide HDACi, which retain their efficacy against the parasite at 10-20 nM, and with better selectivity indexes (SI = 40-60). Interestingly, for analogues related to largazole family, we observed a reversal selectivity of our new HDACi.

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Keywords: *Antiprotozoal agents; Molecular diversity; Medical chemistry;*

Medicinal Chemistry session – I

O-323

POLYOXOMETALATES AS VERSATILE ENZYME INHIBITORS

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Polynuclear metal compounds may have considerable potential as metallic drugs. The most prominent representatives are polyoxometalates (POMs) which have been investigated since the last third of the 19th century. In addition to applications in catalysis, separation, analysis, and as electron-dense imaging agents, some of these substances have been shown to exhibit biological activity in vitro as well as in vivo ranging from anti-cancer, antibiotic, and antiviral to anti-diabetic effects.

Polyoxometalates represent a diverse ensemble of nanostructures with an almost infinite variability of chemical, physical and biological properties. The size of typical covalent bridged cluster compounds is in the range from 1 to 3 nm. The attachment of special surface groups on the periphery of cluster compounds may result in self-assembled non-covalent organized structures larger than 5 nm which are characteristic for biomolecules, such as enzymes. Cells of mammalian organisms are typically 10 to 30 µm. However, sub-cellular organelle dimensions are smaller and range in sub-µm sizes. This comparison of size dimension illustrates that polymetalates are small enough to allow the cell membrane to be penetrated without too much interference. Evidently, some types of polyoxometalates are able to be transported into cells, particularly into mitochondria. However, many of such polyanions are only slightly taken up by cells, obviously caused by negatively charged membranes.

On the way to explore the biological activity of polynuclear cluster compounds, we recently recognised POMs as a new class of potent enzyme inhibitors. Certain polyanionic complexes are able to inhibit extracellular E-NTPDases (ecto-nucleoside triphosphate diphosphohydrolases) that are surface-located nucleotide-hydrolyzing enzymes involved in the regulation of signaling cascades by activating P2 (nucleotide) receptors.

We want to present a brief overview about the potential of POMs as E-NTPDase inhibitors and P2 receptor antagonists.

Keywords: *Enzyme; Inhibitors; Polyoxometalates;*

Medicinal Chemistry session – I

O-324

CYCLAMMONOPROPIONIC ACID- A PROMISING CHELATING SYSTEM FOR RADIOCOPPER ISOTOPES

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A wide variety of radiometal-chelating bioconjugates have been studied intensively to design effective radiopharmaceuticals for diagnostic and therapeutic purposes. Azamacrocycles offer an enormous potential to achieve highly stable radiometal complexes and allow the covalent attachment of targeting and/or fluorescence units at the ligand skeleton. In this context, 1,4,8,11-tetraazacyclotetradecane-1,4,8,11-tetraacetic acid (TETA) is quite often used for the development of copper-based target-specific radiopharmaceuticals, although demetallation and transchelation occur in biological systems. In contrast, radiolabeling of propionic acid analogues has not been reported so far.

An appropriate building block to form very stable complexes with copper(II) is N-mono-(2-(carboxy)ethyl)-1,4,8,11-tetraazacyclotetradecane (Cyclammonopropionic acid, CMPA) which permits the formation of stable radiocopper complexes as well as a facile approach to obtain peptide multimers. An improved pharmaceutical targeting might be utilized due to the multimeric peptide functionalization of the chelating agent. The Epidermal-Growth-Factor-Receptor (EGFR), which is overexpressed on a multitude of tumors, has been chosen as target system to be studied.

Herein, we want to report about coupling reactions of the model dipeptide H-(L)-Leu-(L)-Ala-OH, which is a part of an EGFR-specific peptide, with the cyclammonopropionic acid skeleton. Radiolabeling of CMPA-peptide conjugates with copper-64 indicate high in vitro stability of the complexes formed. So far, this promising behavior may pave the way to develop attractive candidates for radiopharmaceutical applications.

Keywords: *chelates; copper; peptide; radiopharmaceutical;*

Medicinal Chemistry session – II

O-325

C-2 FUNCTIONALIZATION OF PIPERIDINES VIA DIRECTED TRANSITION METAL-CATALYZED SP3 C-H ACTIVATION

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The development of transition metal-catalyzed methods for the direct functionalization of sp^3 C-H bonds is one of the current challenges in organic chemistry.[1] Within this area, the transformation of a C-H bond in alpha-position to the nitrogen atom of saturated cyclic amines is of great importance[2] since such heterocyclic motifs can be found in an impressive number of natural products and marketed drugs. To date, examples of direct C2-H functionalization of cyclic amines using transition metal-catalysis are still rare. The direct functionalization studies published thus far have mainly focused on pyrrolidines and only show (if any) a limited number of piperidine examples.

We have developed a direct Ru-catalyzed C-2 arylation and alkylation protocol which can be used on unsubstituted and substituted piperidines. The arylation protocol employs arylboronate esters and the alkylation alkenes as reagents.[3, 4] The procedures require a directing group on the piperidine nitrogen. We used a pyridine directing group which has always been considered as a non removable group and developed protocols to remove it in a straightforward manner.

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Keywords: *C-H activation; Homogeneous catalysis; Ruthenium;*

Medicinal Chemistry session – II

O-326

DEVELOPMENT AND APPLICATION OF REVERSIBLE ENRICHMENT TAGS FOR NATURAL PRODUCT DISCOVERY

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Although natural product isolation can be a laborious task, it has yielded myriad drug candidates and inspired synthetic chemists for over a century. Considerable advances have been made in separation technology; however, additional methods are needed to streamline drug discovery efforts. Purification of the active components of a crude extract, which often represent less than 1% by weight, is considered a major bottleneck in natural products discovery. Current isolation techniques are dependent upon the physicochemical properties of the molecules such as polarity or charge. These strategies often provide mixed fractions upon purification, increasing the difficulty of bioassay assessment or structural determination of unknown molecules. To address these issues, we have developed a new method to isolate natural products based upon an orthogonal property, their functional group composition. This technique utilizes reversible enrichment tagging reagents, which react chemoselectively with the desired functional group class faciliting enrichment from complex mixtures. Our previous studies yielded the development of a functional group-specific method for enrichment of hydroxyl group-containing natural products based upon the formation of a silyl ether bond. We were then able to extend our developed silicon chemistry to yield a novel diisopropylsiloxane-functionalized resin that chemoselectively captures natural products containing a carboxylic acid moiety. With these two enrichment tags in hand our goal is to isolate previously undiscovered molecules from well-characterized strains of *Streptomyces*. Additionally, work on a third and fourth enrichment tag, one that is chemoselective for the aldehyde or ketone functionality and the phenol, is also under way.

Keywords: *natural products; Immobilization; Solid-phase synthesis; Antibiotics;*

Medicinal Chemistry session – II

O-327

BIOFUNCTIONALISATION AND 64CU-LABELING OF PYRIDINE-CONTAINING TACN LIGANDS FOR SPECIFIC TARGETING OF EGF-RECEPTOR

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The application of radiolabeled peptides in biomedicine is increasing rapidly and offers excellent prospects for the development of target-specific tumor imaging agents. In this perspective, the incorporation of the positron-emitting radionuclide $^{64}Cu^{II}$ into ligand-peptide conjugates would permit the use of positron emitting tomography (PET) for tumor identification. An important requirement is that the resulting radiocopper-ligand complex is both kinetically and thermodynamically stable *in vivo*. We have developed a ligand scaffold based on bis(2-pyridylmethyl)triazacyclononane (DMPTACN) that forms very stable Cu^{II} complexes. This structure allows for the introduction of linker groups, such as carboxylic acids, maleimide or isothiocyanate, thereby facilitating coupling of targeting molecules.

Among many characteristic targets of cancer tissue, the epidermal growth factor receptor (EGFR) is one of the most important mediators involved in the development of highly malignant tumors. This surface receptor is overexpressed in several tumor entities. The altered expression of EGFR during tumor growth, invasion, and metastasis present an interesting molecular target for tumor diagnosis and therapy.

Meanwhile, some specific peptides are identified capable of recognition EGFR-rich cancer tissue. Among these, the hexapeptide D4 (Leu-Ala-Arg-Leu-Leu-Thr) has been described. We want to present the synthesis of a DMPTACN-peptide conjugate, applying thiourea coupling of the hexapeptide D4 by a DMPTACN isothiocyanate derivative. Radiochemical and radiopharmacological properties will be reported. *In vitro* binding characteristics of the $[^{64}Cu]Cu^{II}$-labeled DMPTACN-peptide conjugate in EGFR overexpressing cancer cells (FaDu, A431) using an immunoprecipitation protocol point to specific interactions.

Keywords: *Copper; Imaging agents; Radiopharmaceuticals;*

Medicinal Chemistry session – III

O-328

MOLECULAR RECOGNITION AT PROTEIN SURFACES

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There is no doubt that proteins can be considered as privileged targets for binding of small ligands. In this context the design of ligands able to disrupt protein-protein interactions is emerging as an even more relevant issue. The breakthrough concept that proteins function as a contact network rather than as independent individuals is not only one of the most important advances in our comprehension of living systems, but also translates to a new era in drug discovery. The few reported examples of diseases caused by “impolite” protein social behavior certainly represent only the tip of the iceberg. Therapeutic intervention through molecules designed to selectively modulate the strength and specificity of protein-protein interactions is becoming a reality. This will not only feature molecules with inhibitory capacity: equally or even more interesting are those compounds which can rescue pre-established interactions or structures whose loss results in disease.

Protein-protein interactions are the result of an ensemble of exquisitely regulated molecular recognition events that take place at protein surfaces. This can be referred to as a ‘protein recognition code’. In order to understand protein-protein interactions and to achieve the efficient design of molecules with the capacity to modulate these protein-protein interactions, it is necessary to decipher this molecular recognition code, the language that proteins use to communicate. Unfortunately, progress in this field is highly unsatisfactory. Indeed, we are not completely illiterate, in the sense that we know the letters of this alphabet. They are the non-covalent interactions, such as hydrogen bonds, electrostatic interactions, ?-cation interactions, Van der Waals forces, and the others. However, we could be compared with a child who is learning to read and attempts Dickens’s Oliver Twist.

Keywords: *NMR; Protein surface; Protein; Peptide; Molecular recognition;*

Medicinal Chemistry session – III

O-329

DUAL ANTICOAGULANT/ANTIPLATELET POLYSULFATED SMALL MOLECULES: A MEDICINAL CHEMISTRY CASE-STUDY

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With the increasing rates of cardiovascular diseases, the need for new antithrombotic drugs is considered of great importance since many of the current drugs are insufficiently effective, often affected by severe adverse effects and require routine monitoring. The search for new alternatives to heparins with a well defined composition associated to feasible synthesis is a strong challenge to medicinal chemists. Thus, a new strategy was designed by the hybridization of an oligo-sulfated moiety with a small-molecule scaffold.Polysulfation of carbohydrate-small molecules used as venotropic agents or nutraceutics was achieved with triethylamine:SO_3 adduct by conventional heating and/or microwave irradiation. The anticoagulant activity was evaluated in human plasma (APTT, PT, and TT clotting times) and in human whole blood (thromboelastography). Enzyme inhibition assays were performed against factor Xa, thrombin, and antithrombin III. Platelet aggregation induced by different agonists was evaluated in whole blood (platelet aggregometry). Three representative compounds were administered intraperitoneally in mice (150 μmol/kg) to measure clotting times and transaminases levels.Eighteen polysulfated small molecules were successfully obtained. The polysulfated compounds prolonged the clotting times and some structure-activity relationships could be inferred, particularly related to the number of sulfate groups. The most active compounds were rutin and 3,6-(*O*-β-glucopyranosyl)xanthone persulfates exhibiting double concentration values in the micromolar range. Human whole blood also became hypocoagulable, and there were no signals of fibrinolysis. While inactive against thrombin, some derivatives showed selectivity for factor Xa (directly or with antithrombin III). Some sulfated compounds inhibit both arachidonic acid and ADP-induced platelet aggregation. *In vivo*, compounds showed a rapid onset of action and a sustained duration of anticlotting effects with no signals of acute hepatic toxicity. A new class of small-molecules with dual anticoagulant/antiplatelet activity was identified and might offer an opportunity, in contrast to known antithrombotic agents, for the treatment of both venous and arterial thrombosis.

Keywords: *Medicinal Chemistry; Drug Discovery; Glycoconjugates; Heterocycles; Polyanions;*

Medicinal Chemistry session – III

O-330

SYNTHESIS OF PIPERINE ANALOGS AS GABAA RECEPTOR LIGANDS

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Black pepper is traditionally used in Asian folk medicine as antiepileptic, antianxiety, sedative, and sleep inducing preparation. One of the ingredients of *piper nigrum*, it's natural pungent alkaloid piperine, was recently identified as a positive allosteric modulator of the $GABA_A$ receptors, the major inhibitory neurotransmitter receptors in the brain.[1] The importance of $GABA_A$ receptors as a drug target and the side effect profile of drugs targeting this receptors at present result in a unbowed demand for new scaffolds.

This study is dedicated to the optimization of the piperine scaffold in terms of ligand potency. A number of 106 derivatives of natural product piperine were synthesized. Compounds were tested for $GABA_A$ receptor activity using a two-electrode voltage clamp essay on *Xenopus laevis* oocytes. In an early stage of the project the amide functionality was modified. Here, the di-*n*-propyl, di-*iso*-propyl and di-*n*-butyl amides were identified as the most efficacious residues. With this knowledge, the modification of the double bond system of the natural product was approached. Under application of transition metal catalyzed cross coupling reactions derivatives with 1,2-, 1,3- and 1,4-substituted phenylene, 1,5-naphthalene and 2,5-thiophene as substitute for the double bond system were synthesized. The aromatic benzodioxole ring system was extended to naphtho[2,3-d]dioxole, incorporating one of the double bonds. Here, new and efficient synthetic routes, involving aryne chemistry or iridium catalyzed direct borylation reactions, to 5- and 6-substituted naphtho[2,3-d]dioxoles were developed and applied in the synthesis of piperine derivatives.

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Keywords: *Medicinal chemistry; Ion channels; Natural products;*

Medicinal Chemistry session – III

O-331

DESIGN AND SYNTHESIS OF SMALL MOLECULES AIMED AT NEW ANTIBIOTICS

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Since the 1960s, defeating antibacterial resistance has mainly relied on the modification of existing antibiotics. It has appeared, however, increasingly difficult to come up with modifications that evade resistance without sacrificing activity and as a result, the pressure for finding new classes of antibiotics is higher than ever before. In this respect, the discovery of potent new antibiotics such as platencin represented a potential breakthrough in antibiotic research. Platencin shows broad-spectrum Gram-positive antibacterial activity and acts on the type II bacterial fatty acid synthesis. However, the pharmacokinetic properties are rather poor and preclude use as an antibiotic drug. To investigate whether platencin can be turned into a successful drug, the development of analogues is a pivotal first step.

In this lecture, synthetic studies directed toward the synthesis of (–)-platencin and several analogues will be described. Furthermore, a recently developed entirely new strategy to disrupt bacterial fatty acid synthesis, based on pantothenic acid derivatives, will be highlighted.

Keywords: *antibiotics; total synthesis; platencin; fatty acid biosynthesis; platensimycin;*

Medicinal Chemistry session – IV

O-332

SMALL MOLECULE MEDIATED REGENERATIVE MEDICINE – NOVEL LEAD COMPOUNDS FOR CARDIOMYOGENESIS

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Regenerative Medicine is understood as one of the most promising therapeutic approaches to alleviate a multitude of diseases. While there is significant progress in the experimental development of this approach related to gene therapeutic intervention often in combination with employing embryonic stem cells, the regulatory implications of such therapies are yet unclear and ethical aspects represent a major obstacle in the further development of such strategies. Hence, small molecules capable to affect cell differentiation towards particular tissues have received significant attention, as the prospect of employing such agents in regenerative medicine seem highly attractive.

Within the past years we have been developing several compounds capable to trigger differentiation of certain progenitor cells towards particular tissues otherwise difficult to regenerate. This particular case study aims at the development of novel lead structures for cardiomyogenesis. We will disclose recent results on the identification of heterocyclic scaffolds capable to efficiently induce differentiation towards functional cardiomyocetes starting from embryonic or progenitor cells, ultimately leading to independently beating heart cells. Considering the fact, that cardiac infarctation represents one of the major death causes in the developed world, the prospect of tissue regeneration of damaged heart muscle tissue offers a highly innovative perspective of regaining heart function, as this organ in not capable to functional repair on its own.

Synthetic approaches towards the individual target compounds exploited modular strategies based on metal assisted catalysis, in particular sequential coupling strategies (C-C, C-N, and C-H activation). Optimization of functional decorations of the particular heterocyclic scaffolds will be discussed in detail.

Keywords: *Medicinal chemistry; Heterocycles; Drug design; Cross-coupling;*

Medicinal Chemistry session – IV

O-333

DUAL-LABELED PEPTIDE DENDRIMERS FOR FLUORESCENCE AND SPECT/CT IMAGING OF CXCR4-EXPRESSING CELLS AND TUMORS

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The chemokine receptor 4 (CXCR4) is over-expressed in more than 23 types of cancer were it plays a role in, among others, the metastatic spread. Therefore, it is an emerging biomarker in the field of tumor imaging.[1] CXCR4 is also used as a target for cancer therapy and chemosensitization. The 14 amino acid-containing disulfide-bridged Ac-TZ14011 cyclic peptide has proven to be a potent inhibitor of CXCR4.

We have synthesized monomeric, dimeric and tetrameric Ac-TZ14011 dendrimers. These dendrimers were labeled with a multimodal (hybrid) label, consisting of a Cy5.5-like fluorophore and a DTPA chelate for indium labeling. This combination allows for both (in vitro/in vivo) fluorescence imaging and (in vivo) SPECT/CT imaging.

Confocal microscopy revealed that all three multimodal dendrimers were membrane-bound at 4 degrees Celsius, consistent with the location of CXCR4. The unlabeled dimer and tetramer had a somewhat lower affinity for CXCR4 than the unlabeled monomer. However, when labeled with the multimodal label the CXCR4 affinity of the dimer and tetramer ($K_D = 93.1$ nM and 80.5 nM, respectively) were considerably higher compared to the labeled monomer ($K_D = 186.9$ nM). SPECT/CT tumor visualization in mice was possible with all three compounds. Biodistribution studies revealed that the additional peptides in the dimer and tetramer reduced nonspecific muscle uptake compared to the monomer, resulting in tumor-to-muscle ratios of 7.41 for the dimer and 5.47 for the tetramer. In conclusion, multimerization improved the efficacy of multimodal labeled peptide.[2–3]

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Keywords: *Peptides; Dendrimers; Imaging agents; Fluorescent probes; Radiochemistry;*

Medicinal Chemistry session – IV

O-334

DEHYDRO-BETA-AMINO ACID CONTAINING PEPTIDOMIMETICS AS INTEGRIN RECEPTOR LIGANDS

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Design and synthesis of non proteinogenic amino acids represent a central issue for chemists working in the area of medicinal chemistry and among them, unsaturated β-amino acids have attracted high interest as valuable intermediates in the synthesis of dehydropeptides, allowing the preparation of conformationally constrained sequences with improved biological activity and selectivity. In particular, we are interested to the synthesis of receptor-selective peptides and peptidomimetics, mimicking the RGD motif, present in a wide number of extracellular matrix proteins. These ligands bind to $\alpha_v\beta_3$ and $\alpha_5\beta_1$ integrins, a large family of heterodimeric transmembrane glycoproteins, involved in the pathogenesis of several diseases, such as atheroschlerosis, osteoporosis, cancer and a variety of inflammatory disorders. In view of the application as central cores of peptidomimetics, we have developed synthetic strategies for the preparation of linear and cyclic dehydro-β-amino acids, using alkylidene acetoacetates and malonates as starting materials.

The use of five membered heterocycles as proline analogues has been extensively explored to induce conformational restraints in peptidomimetics. We have recently developed the synthesis of 5-hydroxyisoxazolidine-4-carboxylate, and related functionalized isoxazolines, as heterocycles containing the dehydro-β-amino carboxylate fragment. Lewis acid induced Michael addition of hydroxylamine derivatives to alkylidene acetoacetates, followed by intramolecular hemiketal formation, allowed to obtain a small library of functionalized isoxazoline-based integrin ligands.

Moreover, transformation of alkylidene derivatives into the corresponding allylic carbonates furnished linear dehydro-β-amino acids, through regio- and stereoselective allylic amination in the presence of palladium and iridium catalysts. Introduction of an allylamino moiety through the S_N2' reaction, gave also access to an intermediate containing two unsaturations, thus suggesting that RCM could be a valuable tool for the preparation of dihydropyrrole scaffold.

Decoration of the dehydro-β-amino acid cores with the proper appendages to mimic aspartate and arginine side chains, afforded structures possessing excellent receptor affinity as confirmed by cell adhesion inhibition assays.

Keywords: *Ligand design; Michael addition; Amino acids; Peptidomimetics; Cancer;*

Medicinal Chemistry session – IV

O-335

DISCOVERY OF NEW HER2/EGFR DUAL KINASE INHIBITORS BASED ON ANILINOQUINAZOLINE SCAFFOLD AS POTENTIAL TARGETING ANTI-CANCER AGENTS

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Dual inhibitors of human epidermal growth factor receptor (HER2) and epidermal growth factor receptor (EGFR) have been investigated for breast, lung, gastric, prostate, and other cancers. Herein, we designed and synthesized anilinoquinazoline derivatives bearing bulky such as arylpyridinyl and arylpyrazolyl moieties at the 4' position of the anilinoquinazoline, as HER2/EGFR dual kinase inhibitors, capable of fitting into the receptor ATP binding sites. Binding modes of the designed compounds in the ATP binding sites for both EGFR and HER2 was carried out by means of docking study which demonstrated distinctive binding mode for these compounds with MET793 and MET 801 at the hinge region of both EGFR and HER2 respectively. The synthesized compounds were further tested for their inhibitory activity on EGFR and HER2 tyrosine kinases. Two 2-imino-1,2-dihydropyridine derivatives displayed the most potent inhibitory activity on EGFR with IC_{50} equal to 2.09 μM and 1.94 μM respectively and for HER2 with IC_{50} equal to 3.981 μM and 1.036 μM respectively. Furthermore, antiproliferatve activity against MDA-MB-231 breast cancer cell lines, known to overexpress EGFR. showed an IC_{50} range of 0.5–0.6 μM.

Keywords: *antiproliferation; bioorganic chemistry; drug discovery;*

Medicinal Chemistry session – IV

O-336

POLYSACCHARIDE-ASSISTED CLUSTERING OF PALLADIUM NANOPARTICLES

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Clusters of metal nanoparticles (NP) functionalized by biomacromolecules are used in a rapidly emerging field of nanobiotechnology. Palladium NPs are noticeable for forming various self-assembled structures, though the effect of polymer templates on the (Pd)NPs aggregation is poorly understood. Recently, (Pd)NPs were obtained by using arabinogalactan (ARB) as the nanoreactor, reducing Pd ions to a zero-valent state, and the stabilizing agent preventing the NPs from aggregation.[1] We study the NPs clustering in the ARB@(Pd)NP colloids by dynamic (DLS) and static (SLS) light scattering at 632.8 nm, resonantly enhanced by surface plasmon resonances (SPR) of NPs. Broad size dispersion of spherical ARB@(Pd)NP aggregates is evidenced by scanning and transmission electron microscopy.[2, 3] The red shift of the SPRs with the colloidal size increasing is demonstrated by the difference UV/Vis spectroscopy of the colloids fractionated by centrifugation. The proximity of SPR of the largest aggregate to the incident light wavelength determines their most efficient role in scattering. Therefore, SLS and DLS probe the gyration (R_g) and hydrodynamic (R_h) radii of largest colloids. R_g of the colloidal aggregate is governed by the NPs' distribution because the NP's density is much higher than that of the polysaccharide. The structure-sensitive ratio $R_g/R_h \approx 1$ points out that the NPs form the spherical layer at the colloidal surface. Negative colloidal zeta-potentials show that the NPs layer is covered by a layer of ARB. Zero scattered light depolarization also indicates the spherically symmetric distribution of Pd nanoparticles within colloidal aggregates. Spherically symmetric ARB@NP(Pd) colloids with the shell of NPs at the surface can serve for creating new NPs' self-assemblies.

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Keywords: *Nanostructures; Nanoparticles; Colloids; Aggregation;*

Medicinal Chemistry session – IV

O-337

MONOCYCLIC BETA-LACTAMS AND CYSTIC FIBROSIS: FACING ANTIOXIDANT AND ANTIMICROBIAL ACTIVITY OF N-THIOMETHYL-AZETIDINONES

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Beta-lactam antibiotics are the main class of agents used to treat bacterial infections. Notwithstanding their pivotal role, the treatment of bacterial infections became tangled because of the increasing emergence of multidrug-resistant microorganisms.*Staphylococcus aureus* (SA) is a major pathogen causing significant morbidity and mortality in both community- and hospital-acquired infections. Many staphylococcal infections which tend to become chronic, are associated with multiple recurrences and developed antibiotic resistance. This concern is important in the cystic fibrosis (CF) disease where a persistent colonization of pathogen bacteria occurred and a constant use of antibacterial agents selected resistant strains.

We actively contributed to the field with the design and synthesis of new monocyclic beta-lactams as scaffolds for antibiotics against resistant bacteria and as effective enzymatic inhibitors against HLE, MMPs, HDACs, and as antiaggregating agents.

We recently evaluated a series of *N*-thiomethyl-azetidinones against Gram-positive and Gram-negative bacteria, particularly methicillin resistant SA strains (MRSA) from clinical isolates of CF patients. The combination of specific groups on the beta-lactam ring strengthened the potency against MRSA.

We also evaluated the antioxidant activity and redox potentials of the new beta-lactams with the aim to develop new promising molecules which associated antibacterial and antioxidant activities able to contrast the adverse conditions in CF due to MRSA and extensive epithelial damages by chronic pulmonary oxidative stress.

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Keywords: *Antibiotics; Lactams; Synthesis Design; Inhibitors; Antioxidants;*

Medicinal Chemistry session – IV

O-338

SELECTIVELY LABELLED BETULININES

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Betulin and betulinic acid belong to the group of natural triterpenoids.Together with their semisynthetic derivatives form basis for extensive medicinalresearch, because they have shown various biological activities,[1] e.g.:antiviral, anti-inflammatory, antimicrobial activities, hepato- andcardioprotective effects; and reveal a great potential for pharmaceuticalapplications when their cytotoxic and anti-HIV activities were described.[1, 2, 3] Betulinines, as we named that group of derivatives, have provedmultispectral cytotoxic activity on the panel of 10 cell tumor lines ofdifferent histogenetical origin, including multidrug resistance.[1, 2, 3]

One of our leading compound 3β,28-diacetoxy-18-oxo-19,20,21,29,30-pentanorlupan-22-oicacid fast and selective apoptosis of tumor cells,[3] comparable toconventional anticancer drugs. Selectivelylabelled analogues of the most cytotoxic active compounds are used for theinvestigation of mechanism of action and binding interactions. Until the present time hasbeen synthesized over twenty deuterated, five tritiated and six compoundslabelled with ^{15}N, which were fully characterized by all availablespectral data.

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Medicinal Chemistry session – IV

O-339

DEVELOPMENT OF MULTI-MODAL MOLECULAR PROBES FOR BETA-CELL IMAGING

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According to the World Health Organization 346 million people worldwide have diabetes. The patho-physiology of diabetes is complex; it results from the impairment of insulin secretion and/or function. Type-I diabetes is characterized by the loss of most insulin producing Beta-cells, leading to the loss of endogenous insulin secretion. Type-II diabetes is characterized by impaired insulin secretion and insulin resistance, and a reduction of Beta-cell mass. Thus monitoring the changes in Beta-cell mass is of great interest. Glucagon like peptide-1 (GLP-1), an incretin peptide which binds to its membrane receptor (GLP-1R) at the surface of Beta cells is a suitable candidate for imaging.

Therefore, we designed molecular probes using GLP-1 analog exendin-4 as ligand. A fifth generation poly(amido amine) dendrimer (PAMAM) was chosen as the carrier; thanks to its high degree of molecular uniformity, narrow molecular weight distribution, and highly functional terminal surface.

The PAMAM surface was labeled with 5(6)-carboxy-x--Rhodamine-NHS ester to obtain a Rhodamine labeled PAMAM, which was further modified with suitable linkers specific to thiol-maleimide chemistry and oxime ligation. By using these two different strategies probes were synthesized with a loading of 1-5 Exendin-4. An *in vitro* approach using glucose responsive cell-line model (MIN6) for Beta-cell and two non insulin producing cell-lines (PANC1, and HeLa, respectively) were used to challenge our probes and verify their localization and affinities to the GLP1 receptor. Our primary data confirm the specificity of our probes for insulin producing cells and show a similar pattern of localization between our probes and the GLP1 receptor at a nano molar concentration. In this poster we will present the synthesis details of these probes and the imaging studies that are being conducted to test their usefulness for the imaging of Beta-cell both *in vitro* and *in vivo*.

Keywords: *Diabetes; Beta-Cell; Molecular Probes; Molecular imaging;*

Mass Spectrometry in Life Science – I

O-456

TANDEM MASS SPECTROMETRY IN CLINICAL ENZYMOLOGY: RECENT PROGRESS IN NEWBORN SCREENING OF INBORN ERRORS OF METABOLISM

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Lysosomal storage disorders (LSD) represent a group of inherited metabolic diseases caused by malfunctioning of one of the ca. 60 specialized enzymes in the lysosome. Lysosomal enzyme deficiencies result in accumulation of unprocessed substrates (sphingolipids, glycogen, glycosaminoglycans, peptides, etc.) leading to cell death and progressing to organ or system failure.

In the last decade there has been substantial development of treatments for LSD. The currently used therapies are based on enzyme replacement therapies or hematopoietic stem cell transplantation. The common feature of these therapies is that they have the highest success rate if applied before the onset of symptoms characterizing the disease phenotype. This requirement places emphasis on early detection of affected individuals by high-throughput methods such as those used in newborn screening.

Our labs at University of Washington have been developing specific assays of lysosomal storage disorders to be applied to DBS. The assays use synthetic substrates that are converted to products upon incubation with a small punch of a DBS. The products are detected by electrospray tandem mass spectrometry (MS/MS) and quantified by comparing the ion currents from selected reaction monitoring (SRM) with those produced by internal standards, which are either isotopologues or close homologues. There are currently MS/MS assays for the detection of eleven LSD, namely, Gaucher, Krabbe, Niemann-Pick, Fabry, Pompe, mucopolysaccharidoses Hurler, Hunter, Maroteaux-Lamy, Morquio A, and neuronal lipofuscinoses I and II. Progress has been made on a multiplex assay for MPS-III (Sanfilippo A, B, C, and D). The analytical procedures have been validated by an ongoing large-scale pilot program of triplex screening for Fabry, Pompe and Hurler diseases (>80,000 samples) at the Washington State Newborn Screening Laboratory.

Keywords: *mass spectrometry; glycolipids; oligosaccharides;*

Mass Spectrometry in Life Science – I

O-457

THE NOVEL ANTIMICROBIAL PEPTIDE FROM THE VENOM OF SOLITARY BEE MACROPIS FULVIPES AND ITS ANALOGS

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Antimicrobial peptides (AMPs), which are part of the innate defense system of practically all living organisms, are among the most promising lead compounds for developing medicines in the fight against resistant pathogenic bacteria. During recent years we have isolated, determined the structure, prepared synthetically and characterized several novel AMPs from the venom of different species of Hymenoptera. The most interesting AMPs were identified in the venom of wild bees. The novel AMP, named MAC-1, was isolated from the venom of the solitary bee *Macropis fulvipes*. By Edman degradation and mass spectrometry, its primary sequence was established as GFGMALKLLKKVL-NH_2. MAC-1 possesses potent antimicrobial activity against both Gram-positive and -negative bacteria and moderate hemolytic activity against human red blood cells. CD spectra confirmed that MAC-1 can form an amphipathic α-helical secondary structure in the presence of membrane-mimicking substances as sodium dodecyl sulfate or organic solvents like trifluoroethanol. We prepared a series of MAC-1 analogs to study the effect of incorporating D-amino acid into the sequence on antimicrobial and hemolytic activity, α-helicity and serum stability.

Keywords: *peptides; Circular dichroism; Biological activity;*

Mass Spectrometry in Life Science – I

O-458

PREPARATION OF MODIFIED OLIGONUCLEOTIDES BY NICKING ENZYME AMPLIFICATION REACTION

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Nicking enzymes are a class of restriction enzymes which cut one strand of the DNA duplex to produce shorter DNA fragments. One of the major applications of nicking enzymes is in Nicking Enzyme Amplification Reaction (NEAR), which has been reported to rapidly synthetize short oligonucleotides under mild isothermal conditions. The amplification is based on the continuous repetition of two steps: polymerase-mediated primer extension and nicking enzyme-mediated cleavage. The cleaved oligonucleotide is too short to form a stable duplex with the template and leaves the duplex, thus regenerating the initial dimer primer-template.

NEAR has so far been used on an analytical scale for the detection and quantification of DNA. Here, we present a method based on NEAR developed for the preparation of modified oligonucleotides. In the initial experiments the most efficient combination of DNA polymerase and nicking enzyme was established. These enzymes were used for the incorporation of *m*-aminophenyl-modified nucleobases. The reaction temperature, time, and amounts as well as the ratio of both enzymes were also optimized. To evaluate the scope of the optimized procedure, a series of modified $dC^{X}TPs$ bearing various modifications used previously in DNA labelling, protection and bioconjugation was incorporated using three different templates. Thus, three different sequences of 12-mer ONs bearing either one or three modifications were prepared.

Apart from working on an analytical scale, we also transferred the procedure to nanomolar amounts. A protocol for the isolation of pure modified oligonucleotides including a separation on HPLC was developed. The products were characterized by HPLC retention time, UV-VIS spectroscopy and MALDI spectrometry.

Our methodology is complementary to the synthesis of medium-length single-stranded oligonucleotides by PEX followed by magnetoseparation on streptavidine-coated beads. Thus prepared short modified oligonucleotides can find applications as modified primers for PEX and PCR as well as in diagnostics.

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Keywords: *oligonucleotides; DNA cleavage;*

Mass Spectrometry in Life Science – I

O-459

DETERMINATION OF THC METABOLITES IN SALIVA USING GC-MS

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A sensitive analytical method has been developed for the determination of metabolites of THC (Δ9-THC-COOH) in the saliva. In our hands, the method described produced the best reproducibility and the best match for determining metabolites of THC in saliva (1 ±0.05 g). We stable isotope labeled the specimens with deuterium (Δ9-THC-COOH-d9) prior to testing, and thereby could use the resulting compound as an internal standard (ISTD). The resulting substance was subjected to alkaline hydrolysis, afterward solid-phase extraction (SPE) was preformed, followed by derivatization with N,O-bis(trimethylsilyl) trifluoroacetamide (BSTFA). Finally the result was obtained using the GC-MS system, using the Selective Ion Monitoring (SIM) measuring mode. The results of the target and qualifier ions were m/z 371 [100], 473 [25], 488[9] in the case of 11-nor-9-carboxy-Δ9-THC, and m/z 380[100], 479[24], 482[5] in case of 11-nor-9-carboxy-Δ9-THC. During our measurements, the calibration curve was linear between 5 and 100 ng/ml. The Limit of Detection (LOD) was 1.15 ng/mL and the Limit of Quantification (LOQ) was 4.53 ng/ml. During the analysis, we did not notice any interference, either in the determination of 11-nor-Δ 9-carboxy-Δ9-THC nor 11-nor-9-carboxy-Δ9-THC-D9, either in the specific testing nor the selective testing. All the results of the qualifications were in line with the German Standards DIN 32645, which were checked with the B.E.N. computer program.

Keywords: *gas chromatography/mass spectrometry;*

Mass Spectrometry in Life Science – II

O-460

LIQUID CHROMATOGRAPHY/MASS SPECTROMETRY IN ATMOSPHERIC FINE PARTICULATE MATTER AND SECONDARY ORGANIC AEROSOL RESEARCH

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During the past decade considerable progress has been made in our understanding of the fate of biogenic volatile organic compounds (BVOCs), mainly isoprene and monoterpenes, which are emitted in large amounts from the vegetation (estimated at 1150 TgC/year globally) into the atmosphere. Secondary organic aerosol (SOA) formation through ozonolysis or photooxidation (hydroxyl radical-initiated reactions) of these BVOCs has been studied under atmospherically relevant conditions in environmental chambers. Molecular characterization of organic aerosol constituents is important because it allows one to gain insights into aerosol sources and the underlying mechanisms of SOA formation and transformation (or aging). A common term to denote analytically accessible organic compounds, which provide this valuable information in a complex matrix such as ambient fine aerosol containing biogenic SOA, is “tracer”.

Emphasis will be given to the chemical characterization of several novel SOA tracers from the photooxidation of isoprene, monoterpenes (i.e., α-pinene, β-pinene, and Δ^3-carene) and a green leaf volatile (i.e., cis-3-hexenal), using liquid chromatography/negative ion electrospray ionization mass spectrometry [LC/(–)ESI-MS], high-resolution MS, and detailed interpretation of MS data. The structural elucidation of the following SOA tracers will be addressed:

- terpenylic acid and related lactone-containing terpenoic acids, which are early photooxidation products;
- di-esters formed between pinic acid and terpenylic acid, which are major high-MW products in ambient fine aerosol from forested sites; and
- polar organosulfates derived from isoprene and cis-3-hexenal.

By now the major biogenic SOA tracers in ambient fine aerosol from forested sites have been structurally characterized. This is a prerequisite to develop quantitative LC/MS methodology and perform field studies in the future where time series, day/night chemistry, and dependence on meteorological parameters can be explored in more detail.

Keywords: *structure elucidation; environmental chemistry; oxidation; ozonolysis; mass spectrometry;*

Mass Spectrometry in Life Science – II

O-461

MS-BASED PEPTIDOMICS FOR AUTHENTICATION OF FOOD AND NON-FOOD COMMODITIES

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The authenticity of quality products is an issue of paramount importance in the production of many food and non food products. Authenticity is usually intended as the adherence to defined production methods, the use of particular ingredients (for foods) or raw materials (for non foods) or a well defined place of production. The detection of frauds and the objective assessment of authenticity are essential, also because of the high market prices of the high-quality brand products. In the present communication, it will be shown how MS analysis of proteolytic peptides is a useful tool for rapidly and reliably determining the authenticity of food and non-food products at the molecular level. Proteolytic peptides, generated from the casein breakdown which takes place during the production and the ageing of cheeses, were used as markers for the mammalian species from which the milk for cheese production was obtained. In particular, LC/ESI-MS analysis of homologous, but not identical, proteolytic peptides derived from alfa$_{S1}$-casein allowed to rapidly and reliably assess the presence of cows' milk in cheeses supposedly made only from sheep milk or water-buffalo milk. Marker peptides, derived from enzymatic digestion of gluten extracted from wheat, allowed the determination of the presence of common wheat in flours declared to be made of pure durum wheat varieties. LC/MS analysis also allowed to quantify the amount of common wheat, which, according to the Italian law, cannot exceed 3%. Enzymatic digestion of keratin extracted from textile fibres and peptide analysis by LC/ESI-MS allowed to determine not only the presence of fibres derived from different species (yak, cashmere goat, sheep) but also to assess the relative percentage of usage. In all these cases MS-based peptide analysis turned out to be essential in order to obtain objective data on the authenticity of the specified products.

Keywords: *Peptides; Proteomics; Mass Spectrometry; Liquid Chromatography;*

Mass Spectrometry in Life Science – II

O-462

A NOVEL CAGED CARBONYL FOR BIOMATERIAL MODIFICATION AND CELL PATTERNING

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Patterning cells to mimic the arrangements found in vivo is highly desirable for a number of applications, including tissue engineering. Photolabile protecting groups (PPGs) have been used to "cage" functional groups such as carboxylic acids and amines on biomaterial surfaces.[1, 2] "Uncaging" specific areas by masked exposure to UV light allows cell-adhesive biomolecules to be ligated to the free groups, enabling cell patterning. However, cells are rich in these groups, so sequential patterning of different species is impossible without modification of both the scaffold and existing biomolecules.

A novel bi-functional linker, possessing a "caged" carbonyl (a functional group not naturally found in biology) at one end and a free amine for facile attachment to natural and synthetic biomaterials was synthesized.[3] This molecule was subsequently attached to collagen. Attachment and subsequent PPG loss following UVA exposure (10 minutes) was confirmed by UV/vis spectroscopy, HPLC and mass spectrometry.

Cell adhesion and viability on modified biomaterials was investigated. Collagen films were modified with PPG and photolysed. The presence of PPG on the collagen surface and resultant free carbonyls prevented cell adhesion. Surfaces were treated with a cell adhesive protein (gelatin) chemically modified to incorporate hydrazide functionality. As a control, ligation with unmodified gelatin was attempted. Only selective ligation of hydrazide functionalised gelatin resulted in reintroduction of cell adhesion.

UVA exposure of collagen films and gels using photo-resistant masks resulted in the creation of patterns, visualized *via* treatment with fluorescein-5-thiosemicarbazide. The ability to control cell adhesion and create patterns on modified biomaterials using a novel caged carbonyl has been demonstrated. This approach has great potential for recapitulating natural microenvironments and guiding 3D cell growth with patterned molecular cues.

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2. D. Falconnet et al (2006) Biomaterials 27:3044-63.
3. L. O'Donovan, P. A. De Bank *(in preparation)*.

Keywords: *Materials Science; Photochemistry; Cell Adhesion;*

Mass Spectrometry in Life Science – III

O-463

ENHANCED UNDERSTANDING OF ION CHEMISTRY FOR – AND THROUGH – THE CHARACTERISATION OF PEPTIDES BY MASS SPECTROMETRY AND ION MOBILITY SPECTROMETRY

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The heavy reliance on tandem mass spectrometry of both qualitative and quantitative analyses of the proteomes of both simple and complex organisms has emphasised the importance of understanding the underlying ion chemistry of peptides. Some of the basic concepts are now well established, such as the notion that the multiplicity of charge-driven fragmentation pathways associated with low energy collisional activation of protonated peptides derives from a precursor ion population heterogeneous with respect to site of charge - a situation itself derived from the "mobility" of the ionising proton(s). In many cases, the resulting fragmentation is simple and it is correspondingly straightforward to relate fragment ions to precursor structure. In some instances, however, ion rearrangements may occur which, unless they are understood (or avoided by manipulation of the experiment), may lead to erroneous structural conclusions.

In some instances, for example, rearrangement at the C-terminus results in loss of the C-terminal residue to give ions denoted as (b_{n-1}+H_2O) (where the b_{n-1} ion would represent formally simple cleavage). One such example is the apparent formation of macrocyclic forms of b-ions (derived from peptide bond cleavage and charge association with the N-terminal fragment); subsequent ring opening and further cleavage may afford ions apparently misleading of the original sequence.

The coupling of ion mobility separation with tandem mass spectrometry combines analytical techniques based on orthogonal ion properties (collision cross-section and mass/charge ratio), and allows direct observation of the possible presence of macrocyclic structures, assuming their lifetime is long in comparison with the timeframe of the experiment. This paper reviews observations around this process, and considers factors that favour or disfavour this chemistry.

Keywords: *mass spectrometry; ion mobility; proteomics; gas phase reactions;*

Mass Spectrometry in Life Science – III

O-464

UTILIZATION OF PHOTOACTIVABLE NANOPROBE AND MASS SPECTROMETRY FOR STRUCTURAL DETERMINATION OF CYTOCHROME P450 2B4 AND CYTOCHROME B5 INTERACTION

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Cytochromes P450 (P450) are terminal monooxygenases of mixed function oxygenase system participating in xenobiotics detoxification, drug metabolism and unfortunately also carcinogen activation. Catalytic activity of some P450s is modulated by facultative redox partner cytochrome b_5 which can mediate the second electron transfer in P450 catalytic cycle.

We developed new photolabeling method to expand our structural knowledge of P450 interactions, especially in the region of membrane domains. Three methionines localized in the hydrophobic anchor of cytochrome b_5 were exchanged for methionine photoactivable analog during recombinant expression. After its photoactivation, covalent bond to proximal amino acid is formed fixating potential interaction. Photoactivable cytochrome b_5 was employed as a probe for P450 2B4 membrane topology mapping. We reconstituted *"in vitro"* both cytochromes in lipid membrane, UV illuminated the mixture and electrophoretically separated formed reaction products. Detected P450:cytochrome b_5 complexes were most likely in molar ratios 1:1, 1:2 and 2:1 according to molecular weight standards. Afterwards, they were cut off the gel and proteolytically digested. Resulting peptide mixture was analyzed employing high resolution LC-FT-ICR mass spectrometry.

We identified cytochromes' amino acids interacting in the lipid membrane environment and like so directly confirmed interaction of studied proteins' membrane helixes for the first time. Depending on experimental approach of *"in vitro"* protein reconstitution the different types of cytochrome b_5 binding to the membrane is supposed according to our acquired mass spectrometric data of covalently cross-linked peptides.

Obtained structural information is utilized for *"in silico"* refinement of proteins' interaction models, their *"in vitro"* reconstitution protocols validation and also certification of pharmacological and toxicological tests carried on this system.

Acknowledgement: *Supported by GACR (P207/12/0627 and 305/09/H008) and the Charles University project UNCE #42.*

Keywords: *Cytochromes; Membrane proteins; Photoaffinity labeling; Mass spectrometry; Structure-activity relationships;*

Mass Spectrometry in Life Science – III

O-465

MASS SPECTROMETRIC INVESTIGATION OF IN VITRO SYNTHESIZED POLYPHENOLIC BIOPOLYMERS: LIGNINS AND EUMELANINS

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MALDI-ToF mass spectrometry has shown to be an extremely useful technique for the structural characterization and elucidation of the biosynthetic pathway for the *in vitro* formation of the polyphenolic biopolymers lignins and eumelanins. Eumelanins and lignins share quite similar biosynthetic pathways. The monomeric starting materials are polyphenolic in nature; the polymerization processes are both triggered by oxidative enzymes and are known to proceed according to radical steps; the final polymers themselves, highly heterogeneous in their overall structure, are totally insoluble and do not degrade by any conventional chemical and/or enzymatic treatment.

In particular by MALDI-ToF mass spectrometry we were able to fully characterize a model coniferyl alcohol lignin (the so-called dehydrogenative polymerizate, DHP), produced by the action of peroxidase/H_2O_2 on the alcohol monomer in different reaction media, namely: pure buffer, organic solvent mixtures, and in water under homogeneous conditions guaranteed by the presence of a micellized cationic surfactant. The structural features of the polymers obtained under such reaction conditions allowed us to drive some conclusion as to its *in vitro* biosynthesis.

Based on the grounds of the results on lignin biosynthesis, an unprecedented breakthrough into the mechanism of synthetic eumelanin buildup came from a detailed investigation of the oxidative polymerization of DHI (5,6-dihydroxyindole) and its *N*-methyl derivative (NMDHI) by linear and reflectron MALDI-MS. Regular collections of oligomers at increasing masses, spanning the entire *m/z* range up to 5000 Da (>30-mer) and 8000 Da (>50-mer) for the two buiding blocks respectively, were disclosed. It is the first time that the in vitro polymerisation of dihydroxyindoles to form synthetic eumelanins is explored up to its high mass limits, giving at the same time information on the polymerisation mode, whether it follows a stepwise pattern (being this the conclusion in our case) or a staking sequencing of small sized entities.

Keywords: *Mass spectrometry; Natural Products; biopolymers;*

Mass Spectrometry in Life Science – III

O-466

DIFFERENTIAL ANALYSIS OF AN EXOSOME PROTEOME

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Myeloid derived suppressor cells (MDSC) are hypothesized to contribute to increased cancer risk by suppressing anti-tumor immunity. Inflammation has been observed to enhance MDSC activity and to increase cancer risk. To determine how inflammation drives MDSC function, mass spectrometry-based proteomic strategies have been employed to identify and compare proteins in exosomes shed by MDSC developed in the tumor environment in mice bearing BALB/c mouse-derived 4T1 mammary carcinomas, and in mice exposed to the pro-inflammatory mediator interleukin-1β. Eight hundred and seventy-five proteins were identified in exosomes (80 μg) from conventional MDSC using 1D gel electrophoresis, a bottom-up proteomic workflow and a meta-search program (htts://edwardslab.bmcb.georgetown.edu/PepArML/) that integrates MASCOT and six open source search engines. Protein identifications were based on two or more peptides with a false discovery rate < 10%, and were compared to entries in the international exosome database ExoCarta.org. A quantitative comparison of protein abundances in exosome samples from conventional and inflammatory MDSC (combined total 48 μg) was carried out using the iTRAQ protocol. Four repetitive analyses were made using a three hour gradient on a C-18 nanobore column in a Shimadzu Prominent HPLC interfaced to a Thermo LTQ-orbitrap. Isotope ratios were automatically determined using Proteome Discoverer v.1.2 (Thermo Fisher Scientific). Of 1164 unique ratios determined, the relative abundances of 87 proteins were found to be altered greater than 2-fold. These proteins will be discussed, along with analyses of ontology and function.

Keywords: *proteomics; mass spectrometry;*

Nanochemistry, nanotechnology and nanostructured materials – I

O-061

METAL-ORGANIC FRAMEWORKS WITH DYNAMIC INTERLOCKED COMPONENTS

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A variety of artificial molecular switches and machines have been reported that are based on the relative motion of the components of mechanically interlocked molecules (MIMs). However, these and other elaborate systems only operate in solution or in a condensed phase where the molecular devices are randomly dispersed and their motion incoherent. If these tiny devices could be organized in a predictable and orderly manner, the ideas of creating ultra-dense molecular-based memory or controlling electronic properties of materials at the molecular level would be very much closer to realization. One way to achieve a higher level of molecular organization and coherency would be to precisely place the "soft" dynamic molecular components that undergo motion (*e.g.*rotation or translation) into the pores of metal organic framework (MOF) materials In this way, the soft MIM would be clearly separated from the "hard" structural skeleton of the MOF that holds it in place. If this could be accomplished, the small size of a MIM unit (~1 nm^3) and the regularity of a MOF framework would allow for an incredibly high density of dynamic components in a material: ~10^{21} per cm^3. The ability to arrange mobile and functional molecular components in a highly dense and predictable array is a crucial step towards the generation of solid-state devices with multiple functions and properties. This presentation will describe our newest results in the design, synthesis and characterization of MOFs with mechanically interlocked components.

Keywords: *Metal-organic frameworks; Rotaxanes;*

Nanochemistry, nanotechnology and nanostructured materials – I

O-063

PREPARATION OF ORDERED METALLIC NANOSTRUCTURES FOR THE INVESTIGATION OF NONLINEAR OPTICAL PROCESSES

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In the last years there has been an increasing interest in the nonlinear optical properties of metallic nanostructures. Assemblies of noble metal particles support local surface plasmon oscillations leading local field enhancement in such systems. This enables us to study multiphoton processes at relatively weak excitation power.

Though lithographic methods yield well-defined nanostructures of various morphologies in the micrometer range, the preparation of large arrays of ordered metallic structures by self-organization of nanoparticles appears to be favorable. This is because the nanoparticle approach yields structures with dimensions well below 100 nm on areas reaching up to square centimeters. Gold nanoparticles of different size and shape are prepared by colloidal chemistry. These are arranged in arrays of ordered structures by self-organization on sapphire substrates and characterized by scanning electron microscopy. The controlled distance between the nanoparticles is adjusted by variable size organic ligands or the application colloidal masks.

For the excitation of the plasmonic nanostructures 80 fs, 800 nm pulses from a Ti:sapphire oscillator were used. Multiphoton processes, such as the two-photon photoluminescence, second and third harmonic generation were investigated in order to characterize the nanostructures and to map out and optimize their plasmonic field enhancement.

Keywords: *Nanostructures; Nonlinear optics; Self-assembly;*

Nanochemistry, nanotechnology and nanostructured materials – I

O-064

MIXED AEROGELS FROM METAL AND SEMICONDUCTOR NANOPARTICLES

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Self-assembled structures are currently of great interest for nanochemistry and chemical nanotechnology. Aerogels consisting of nanoparticles combine promising advantages like high porosity, low density and huge internal surface, whilst retaining the unique properties of their building blocks like quantum-confined optics and catalytic behavior.

Following the recent success in fabrication of new types of aerogels from semiconductor and noble metal nanocrystals, we demonstrate the water-based formation of mixed aerogels consisting of strong emitting, thiol-capped CdTe nanoparticles and thiol-functionalized gold seeds. The formation is carried out by photochemical treatment and supercritical drying resulting in homogeneous and voluminous monoliths.

The composition and topography of the gel was examined by SEM/EDX and TEM proving the highly porous architecture and the control of particle ratios in the network through the initial colloid mixtures. Optical behavior was studied by diffuse reflection and fluorescence spectroscopy verifying the retained optical properties. With increasing metal ratio the fluorescence intensity is decreased due to the quenching of the metallic system on the fluorescence process. By carrying out lifetime measurements of the produced gels this effect was examined. Porosity measurements by nitrogen adsorption characterized the highly porous gel network with specific internal surfaces of 170 m^2/g which is in good accordance to porosity values of such structures found earlier.

The formation of those gels provides a controllable method to produce highly porous hybrid materials of special interest for applications in nanoplasmonic devices and photocatalysis

Keywords: *nanoparticles; sol-gel processes; mesoporous materials; photooxidation; heterogeneous catalysis;*

Nanochemistry, nanotechnology and nanostructured materials – II

O-065

THREE-DIMENSIONAL DNA NANOSTRUCTURES FOR BIOLOGICAL AND MATERIALS APPLICATIONS

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Three-dimensional structures made of DNA hold the potential to encapsulate and release drugs, selectively encage nanomaterials, regulate the activity of proteins, and assemble networks for catalysis and biomolecule crystallization. A number of strategies for DNA construction have been developed, through weaving together DNA strands into tiles, or stapling a DNA strand into origami structures. Our group has been examining a different approach to build DNA nanostructures, in which synthetic molecules are used to control and modify DNA self-assembly.

We will describe the use of this approach to generate 3D-DNA structures, such as DNA cages and nanotubes, with deliberate variation of geometry, size, single- and double-stranded forms, permeability and length. These can be dynamically switched to different internal volumes, and can be 'opened' or closed with specific DNA strands. The size-selective encapsulation of gold nanoparticles within these host structures and the release of this cargo when specific DNA strands are added will be shown. Moreover, these compact 3D-DNA structures can travel across the plasma membrane of a number of mammalian cells, without the aid of any transfection reagents. The molecules shown here represent a new class of selective cellular probes and drug delivery tools, and can assist the development of nucleic acid therapeutic routes. Finally, the use of these cages for the 3D-organization of synthetic polymer chains in their core or corona will be described.

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Keywords: *DNA Structures; Supramolecular chemistry; Nanostructures; Drug delivery;*

Nanochemistry, nanotechnology and nanostructured materials – II

O-066

SELF-ASSEMBLY AND OPTICALLY TRIGGERED DISASSEMBLY OF DENDRON-VIRUS COMPLEXES

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Nature offers a vast array of biological building blocks that can be combined with synthetic materials to generate a variety of hierarchical architectures. Viruses are particularly interesting in this respect because of their well-defined structure and their possibility to function as scaffolds for the preparation of new biohybrid materials. We have shown that Cowpea Chlorotic Mottle Virus (CCMV) particles can be assembled into well-defined micron-sized objects and be reversed back into individual viruses by a short optical stimulus. Assembly is achieved by employing photo-sensitive dendrons that bind on the virus surface through multivalent electrostatic interactions and ultimately act as molecular glue between the virus particles. Individual virus particles can adopt hexagonal close packing within the complex. Optical triggering induces the controlled decomposition and charge-switching of dendrons, which results in loss of the multivalent interactions and the release of the virus particles. Furthermore, the method is not limited to the virus particles alone, but can also be applied to other functional protein cages, such as magnetoferritin.

Keywords: *Viruses; Dendrimers; DNA; Nanoparticles; Magnetic properties;*

Nanochemistry, nanotechnology and nanostructured materials – II

O-067

SUPRAMOLECULAR FUNCTIONALSIATION OF MWCNTS WITH EU(III) COMPLEXES: NOVEL LUMINESCENT MATERIALS FOR PHOTONIC APPLICATIONS

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The luminescence output of a lanthanide complex (LnC) results dramatically dependent from the local chemical environment and its susceptibility to chemical and photochemical degradation. Moreover, the tendency of these luminescent modules to aggregate in solution inducing multi-chromophoric interactions, dramatically alters the colour quality and the intensity of their emission. In principle self-aggregation, together with similar parasite electronic interactions, can be attenuated by controlling the relative arrangement of the individual luminophores. In this respect, carbon nanotubes (CNTs) revealed an interesting scaffold for the regulated positioning of LnCs. Specifically, as we herein report, we have attempted several non covalent supramolecular methodologies for the arrangement of Eu(III) complexes onto multi-walled CNTs (MWCNTs), leading to novel luminescent materials characterised by the synergetic combination of both the luminescent properties of the LnCs and the mechanical and electrical properties of MWCNTs. These hybrids indeed revealed exceptional features exploitable in both the fields of biology and materials science.

Keywords: *Luminescence; Nanotechnology; Lanthanides; Nanotubes; Supramolecular chemistry;*

Nanoscale particles, cages, sheets and tubes – I

O-068

REACTION AND PROPERTY CONTROL IN SELF-ASSEMBLED COORDINATION CAGES

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Since our first report on a metal-cornered molecular square (JACS, 1990, 112, 5645), we have been working on molecular self-assembly based on coordination chemistry. We have shown the highly efficient self-assembly of various cages and capsules with large cavities. In this talk, focus will be on the cavity-directed reaction and property control of organic molecules, which represent one of the most important features of three-dimentional hosts.

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Nanoscale particles, cages, sheets and tubes – I

O-069

TEMPLATED SYNTHESIS OF MOLECULAR WIRE NANORINGS

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This lecture will discuss the use of templates for building large pi-conjugated macrocycles, and will demonstrate that it is possible to go beyond simple 1:1 template:product stoichiometries to direct the synthesis of very large nanorings using small templates. For example we have synthesized a covalent nanoring consisting of 24 porphyrin units with a molecular weight of 26 kDa and a diameter of 10 nm. This is well into the size range of proteins. The 24 porphyrin units are clearly evident in the STM images, providing excellent confirmation of the structure. The tertiary structure of the nanoring can be fixed by formation of a 26-component sandwich complex with DABCO. Denaturation of this complex is extremely cooperative, and resembles denaturation of a protein. Pi-conjugated nanorings of this type are expected to exhibit unusual electronic and photophysical behavior, and to mimic light-harvesting chlorophyll arrays.

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Keywords: *Porphyrinoids; Molecular electronics; Molecular recognition; Self-assembly; Nanostructures;*

Nanoscale particles, cages, sheets and tubes – I

O-070

GUANIDINIUM BINDING MODULATES GUEST EXCHANGE WITHIN A METAL-ORGANIC TETRAHEDRAL CAPSULE

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In recent years significant attention has been given to the synthesis of new metal-organic capsules. These systems have been used in diverse fields such as molecular recognition, reactivity modulation and catalysis. Our group has previously reported the synthesis of a tetrahedral $[Fe^{II}_4L_6]^{4-}$ capsule, **1**, as tetramethylammonium salt.[1] **1** is water soluble and encapsulates guests such as cyclohexane, P_4 and furan within its hydrophobic cavity.[2] Moreover, the exterior of this capsule is decorated with twelve sulfonate groups that are ideally orientated to undergo hydrogen-bonding with the C_3-symmetric guanidinium cation (Gnd^+).

Herein we demonstrate the use of guanidinium-sulfonate interactions [3] to close the faces of a metal-organic container molecule, resulting in the modulation of guest exchange kinetics between bulk solution and the host's cavity.[4]

Host **1** was prepared as guanidinium salt (Gnd_4**1**). Gnd_4**1** was characterised by NMR spectroscopy, mass spectrometry, elemental analysis, and X-ray diffraction. Kinetic studies of cyclohexane uptake into host **1** in the presence of various Gnd^+ concentrations showed a linear relationship between the amount of bound guanidinium and the rate of guest exchange.

In conclusion, we have demonstrated that it is possible to modulate the kinetics of guest exchange in a self-assembled container molecule by capping its faces with hydrogen-bonded guanidinium cations. Studies of the uptake kinetics for other guests are currently underway.

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Keywords: *Supramolecular chemistry; Kinetics; Water chemistry; Host-guest systems; Hydrogen bonds;*

Nanoscale particles, cages, sheets and tubes – I

O-071

OSCILLATORY TEMPLATE EXCHANGE IN POLYOXOMETALATE CAPSULES: A LIGAND TRIGGERED, REDOX POWERED, CHEMICALLY DAMPED OSCILLATION

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Polyoxometalates are solution-processable molecular metal-oxides with nanoscale structures and they are governed by self-assembly processes. Their facile one-pot syntheses, high conductivity, wide range of composition, size and architecture play an important role in the discovery of new materials and technologies from bottom-up strategies.

Unfortunately, self-assembly processes lack of specific mechanistic details. These details are crucial for the on-going efforts to understand, control, predict and then design multifunctional materials utilizing molecular synthons, with well-defined structure and geometries. Therefore, becomes apparent the necessity to utilize a combination of techniques in a smart and constructive way in order to gain access to the underlying chemistry which will allow better control over the self-assembly process.

In this work we we describe the redox-driven template exchange-oscillation which causes the exchange of the two hetero-atom guests, $(XO_4)^{3-}$, contained within the $\{M_{18}O_{54}(XO_4)_2\}^{6-}$ capsule ($X_1 = P^V$ and $X_2 = V^V$) for two complete oscillation cycles ($P_2?V_2?P_2?V_2?P_2$) before being 'chemically' damped and we also show that the oscillations can be restarted by 'resetting' the process allowing up to additionally four complete cycles as shown by preliminary *in-situ* UV-Vis experiments.[1] The present discovery constitutes the first example of a controlled chemical oscillation in supramolecular chemistry accompanied with major structural rearrangement.

These results bring us one step closer to understanding the formation of self-assembled systems. The findings presented here show the potential of polyoxometalate cluster capsules for the design of "smart" molecules and responsive materials.

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Keywords: *self-assembly; polyoxometalates; nanostructures; mass spectrometry; molybdenum;*

Molecular devices and machines – I

O-198

FROM MOLECULAR SWITCHES TO MOLECULAR MACHINES

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For the best part of 20 years now, the wonder of artificial molecular switches (AMSs) acting as nanomachines has inspired engineers as well as physicists and chemists. Despite the fact that significant progress has been made in the preparation of AMSs of increasing complexity and sophistication, the goal of obtaining useful energy/work from these switches has eluded us for the most part. There have been a few examples of molecules acting as primitive machines. These systems are rudimentary, however, and fall short of performing useful tasks on any length scale, be it on the nano-, micro-, or macroscopic levels. In order to transform AMSs into artificial molecular machines (AMMs), we need to learn (**1**) how the coupling/uncoupling to the environment of AMSs can be achieved and (**2**) how these switches can be organized into hierarchical assemblies in order to perform work at various different length scales. At the single molecule level, the focus should be on harnessing the ineluctable effects of thermal noise. The principle of microscopic reversibility, which prevents a system from doing work on the environment, needs to be circumvented. This goal can be achieved, in theory, by either externally modulating the conditions (stochastic pumping) of a reaction or using a catalyst that can be switched back and forth between different states to drive a reaction away from equilibrium. At the macroscopic level, one of the major challenges inherent in the building of machine-like assemblies lies in the ability to control the spatial ordering of switchable molecules in highly interactive and robust architectural domains in order to maximize the power generated as a result of synchronous switching of individual molecules. The development of AMMs holds promise for addressable nanomaterials, such as "breathing" nanomembranes, "folding" nanosheets, "mechanized" enzyme-like mimics, and even perhaps "responsive" nanorobotic arms.

Keywords: *molecular machines; molecular switches; nanomaterials;*

Molecular devices and machines – I

O-199

PHOTOACTIVATED DIRECTIONALLY CONTROLLED TRANSIT OF A NON-SYMMETRIC MOLECULAR AXLE THROUGH A MACROCYCLE

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The ability to control motion at the nanoscale is of fundamental importance in living organisms, and one of the most difficult challenges in nanoscience. In the last few years different research groups have developed artificial molecular machines able to control the movement of molecules and implemented such systems to make responsive materials and surfaces, to control catalytic processes, and to develop systems capable of controlling the storage of informations and the delivery of drugs upon controlled stimulation. But despite all this advancements, the development of synthetic molecular motors capable of directionally controlled linear or rotary movements is still a big challenge. In this work we show as a simple supramolecular assembly constituted by a dibenzylammonium axle with two different end groups, namely an azobenzene unit at one end and a cyclopentyl unit at the other, can be operated to unidirectionally thread through a crown ether macrocycle, DB24C8, using UV light and potassium ions as stimuli. The described system constitutes a first step towards the realization of an artificial molecular pump and can also be further developed to synthesize molecular linear motors based on rotaxanes and rotary motors based on catenanes. Moreover the described system is characterized by a minimalist design, facile synthesis, convenient switching, and reversibility; all this features constitute essential requirements for future real-world applications.

Keywords: *azobenzene; crown ethers; molecular devices; supramolecular chemistry; hydrogen bonds;*

Molecular devices and machines – I

O-200

A ROTAXANE-BASED SWITCHABLE ORGANOCATALYST

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In biology the activity of enzymes is often modulated by co-factors, phosphorylation, or allosteric binding.[1] Achieving similar control over synthetic catalysts[2] could be useful for influencing both the rate and outcome of chemical transformations, the latter perhaps by switching 'on' and 'off' different catalysts that promote alternative reactions in the same pot. Rotaxane-based molecular shuttles have previously been used for information storage, control macroscopic properties of materials, to do mechanical work and in various controlled substrate-release systems.[3]

Here we show that the positional changes of a macrocycle in a switchable rotaxane can be exploited to conceal and reveal an organocatalytically-active functional group. The design of this switchable rotaxane consists of a dibenzo-24-crown-8 macrocycle and an axle containing both triazolium rings and a dibenzylamine/ammonium moiety,[4] which is able to carry out iminium catalysis.

The catalyst can be switched 'on' or 'off' by addition of acid or base which acts to move the rotaxane ring between the binding sites. When the rotaxane is protonated the macrocycle encapsulates the ammonium group blocking access of reactants to the catalytic site. When the secondary amine of the rotaxane is not protonated, the triazolium groups are the preferred binding sites for the macrocycle and the dibenzylamine group on the axle is exposed and available to perform catalysis.

The switchable catalyst was demonstrated to effectively control the rate of Michael addition of an aliphatic thiol to *trans*-cinnamaldehyde.

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Keywords: *Rotaxanes; Organocatalysis; Molecular devices; Molecular recognition;*

Molecular devices and machines – I

O-201

DESIGN AND SYNTHESIS OF POLYROTAXANES FOR BIMODAL IMAGING

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In the past few years, the development of new methods for bimodal imaging has known a growing interest for the diagnosis and understanding of biological processes.[1] Bimodal imaging agents are designed to foster the advantages of two complementary imaging techniques on a single object. For example, joining a fluorescent probe and a magnetic resonance imaging (MRI) contrast agent combines respectively the spatial resolution of MRI and sensitivity of optical imaging.[2]

In our approach, a supramolecular structure for bimodal imaging based on a polyrotaxane has been designed.[3] The polyrotaxane is based on a water soluble polymer threaded by cyclodextrins functionalized by MRI contrast agent or fluorescent probe. Stoppers could be positioned at the extremities of the polymer chain to avoid unthreading. This supramolecular approach presents the advantages of modularity, flexibility and potential biodegradability. Moreover, the use of biocompatible moieties such as cyclodextrin should permit its use for in vivo studies.

The synthesis of cyclodextrins functionalized by contrast agents, and the design of the corresponding polyrotaxanes will be presented.

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Keywords: *polyrotaxane; bimodal imaging; cyclodextrin;*

Molecular devices and machines – II

O-202

MOLECULAR ROTARY MOTORS

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In our body a fascinating collection of ingenious molecular motors and machines make it possible that our cells divide, that we can use our muscles and that the consumption of ATP can be used to generate force and mobility. A billion times larger than these nanoscale protein motors in Nature are the plethora of macroscopic motors that power the cars and machinery in daily life. The ingenious structures and complex functions present in biological systems offer a great challenge to develop synthetic nanostructured materials with functions controllable at the molecular level. *Molecular motors* stand out among the most challenging goals in nanoscience and will provide the heart of future molecular level machinery. Both linear and rotary motors are shown as well as the principle of a chemical powered molecular motor. Progress in the construction of molecular motors anchored to surfaces, the realization of autonomous movement and the application of molecular motors to perform useful functions is discussed.

Keywords: *molecular motor; molecular machines;*

Molecular devices and machines – II

O-203

AN APPLIED VOLTAGE-TRIGGERED SINGLE MOLECULAR SPIN SWITCH

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Herein we report design and successful synthesis of several homoleptic and heteroleptic Fe-bisterpyridine complexes. Especially the implementation of heteroleptic Fe-bisterpyridine complexes into miniaturized electronic devices is of high interest in the field of molecular electronics due to the complexes' potential capability of acting as applied voltage-triggered single molecular spin switches.

To allow a spin switching behavior on a single molecular level the accordant tailor-made molecules had to be immobilizable between two Au-electrodes. Additionally they had to contain a core Fe(II)-ion exhibiting an externally controllable spin state. Therefore we came up with different heteroleptic Fe-bisterpyridine complexes each bearing a symmetric thiol-functionalized terpyridine ligand to enable the complexes' immobilization between two electrodes. The varying second terpyridine ligand incorporated customizable push-/pull-systems exhibiting a strong dipole moment needed to provide the desired sensitivity of the described system towards an applied electric field. The challenge to assemble the uncommon 4,4''-disubstitution pattern required for the terpyridine core moiety was overcome by the development of an unprecedented synthetic route. We applied Suzuki-Miyaura cross coupling reactions utilizing suitable 4-substituted lithium triisopropyl 2-pyridylborates to form the desired 4,4''-disubstituted 2,2':6',2''-terpyridine ligands. Remarkably this coupling methodology, though inevitably depending on α-boronylated heteroaryls, allows a successful assembly of several 2,2':6',2''-terpyridines avoiding the concurring and usually favored proto-deboronation previously described in literature. Finally a cascade of further Suzuki-Miyaura reactions led to the desired target compounds.

For all Fe-bisterpyridine complexes characterized by X-ray crystallography consistently almost perfect octahedral geometries were revealed indicating the required low-spin configurations of the Fe(II)-ions. In the ongoing physical experiments an alternation of the applied electric field strengths between the Au-electrodes should result in a distortion of the original octahedral geometry towards pseudo-planarity triggered by the alignment of the push/pull-ligand with the externally applied electric field. This should then result in a reversible switching of the Fe(II)-ion's spin state.

Keywords: *Molecular Electronics; Cross-coupling; Tridentate ligands; Spin crossover; Single-molecule studies;*

Molecular devices and machines – II

O-204

DESIGN AND SYNTHESIS OF MOLECULAR DEVICES FOR INSULATING SURFACES

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For many years, one of the key challenges in nanosciences has been the design and synthesis of molecule-devices with electronic (switches…) or mechanical (rotor, nanocar…) functions. These nano-objects are generally well-studied at the single molecule level by Scanning Tunnelling Microscopy (STM) on metallic surfaces. However electronic coupling between the adsorbed molecules and these substrates prevents the study of molecular electronical or photophysical properties. In contrast, recent advances in Non-Contact Atomic Force Microscopy (NC-AFM), which now allows precise imaging at the sub-molecular level, have opened the possibility to explore molecular devices on bulk insulators surfaces[1] and to study electronic and optical properties of nano-objects. Unfortunately, molecules strongly diffuse on these surfaces leading to 3D clustering.

In this context, we design and synthesize molecules prone to be observed as single objects by NC-AFM on insulating surfaces (NaCl, KBr). To do so, we have prepared a family of molecules comprising planar and rigid aromatic cores to facilitate image interpretation, equipped with several alkylated chains with various sizes ending by anchoring groups to maximize the molecule/substrate interaction.[2] The anchoring groups are chemical functions with a strong dipolar moment (ex. nitrile, carboxylic acid...) or local charges (zwitterions). One of these molecules (2,3,6,7,10,11-hexacyanopropyloxytriphenylene) has recently been studied on KBr(001) and results are encouraging to continue in this direction.[3]

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Keywords: *Synthesis design; Click chemistry; Zwitterions; Molecular electronics; Adsorption;*

Molecular devices and machines – III

O-205

DNA NANOMACHINES AND NANODEVICES

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The information encoded in the base sequence of nucleic acids allows the design of DNA nanostructures with emerging properties. This will be exemplified with the following systems: (**i**) The design of different DNA machines, including “tweezers”, a “walker”, a “stepper” and a “crane”, using Hg^{2+}, H^+, and DNA strands as “fuels”. Specifically, the synthesis of two- and three-ring DNA catenanes will be addressed, and the programmed, dynamic and reversible translocation of the catenane rings across pre-designed topologies will be described. The catenane machines will be used as functional units for the programmed organization of different sized Au nanoparticle nanostructures. Machine-dictated switchable plasmonic effects will be discussed. (**ii**) DNA provides an organizing scaffold for controlling chemical reactivity on surfaces. This will be exemplified with the design of a “walker” DNA on surfaces and with the organization of relay/semiconductor quantum dots on the scaffolds as photosynthetic model systems. (**iii**) Catalytic DNAs (DNAzymes) act as isothermal autocatalytic replication machineries that, upon interaction with a target fuel, lead to the self-assembly of catalytic DNA nanowires. Application of the systems for the ultrasensitive detection of DNA will be discussed.

Keywords: *Nanostructures; DNA; Self-assembly; Autocatalysis; Catenanes;*

Molecular devices and machines – III

O-206

ANALOG AND DIGITAL CONTROL OF MOLECULAR FUNCTION BY PHOTOCHROMES

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Photochromes can interact with covalently linked chromophores via energy or electron transfer and modification of electronic coupling. Because these interactions are different for the different isomers of the photochrome, these species may act as digital switches to turn some properties of other chromophores on or off. Molecules constructed in this way can perform logic operations or other binary functions. The inputs and outputs of these molecular devices can all be photonic, which avoids product buildup, a need for physical access for reagents, and other limitations inherent in the use of chemical inputs and outputs. Such molecular digital devices may also be reconfigured to perform other operations by changes in the wavelengths of the inputs and outputs. For example, a molecule capable of carrying out 13 different logic operations has been reported. In addition, ensembles of photochromic molecules can carry out analog control functions. In one example, a photochrome controls the quantum yield of photoinduced electron transfer in an artificial photosynthetic antenna-reaction center, thus mimicking a natural photoprotective mechanism found in cyanobacteria. In another, irradiation of a photochrome with modulated long-wavelength light in turn modulates fluorescence of an attached chromophore at a shorter wavelength. Such function could be useful in reducing interference in fluorescent probe applications.

Keywords: *Photochemistry; Photochromism; Molecular devices;*

Molecular devices and machines – III

O-207

LIGHT-HARVESTING ANTENNAE BASED ON LUMINESCENT DENDRIMERS

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Dendrimers are ideal candidates to build up molecular antennae since a large number of different chromophoric units can be arranged in a nanoobject with a predetermined pattern. Because of their tree-like multi-branched structure, they can also form internal dynamic cavities in which small molecules or ions can be hosted, so that supramolecular structures can be self-assembled. The value of the resulting supramolecular systems relies not only on the total number of self-assembled molecules, but also on the diversity of the components and on the functions resulting from their mutual interactions.

In this view, we have studied self-assembled supramolecular structures, based on dendrimers and metal complexes[1] or molecular clips, which can perform also as sensitizers of lanthanide ions. For example, we have investigated several families of dendrimers containing a 1,4,8,11-tetraazacyclotetradecane (cyclam) core,[2] one of the most extensively investigated ligands in coordination chemistry, to build up metal complexes with dendritic ligands.[2] Particularly interesting results have been obtained in the case of a dendrimer constituted by two cyclam units linked by a photoswitchable azobenzene chromophore and 12 naphthalene units at the periphery. In this dendrimer, the distance between the two cyclam units can be modulated by light stimuli thanks to the presence of an azobenzene moiety which can be reversibly switched between trans and cis isomer by light irradiation. Therefore, the trans and cis isomers display different coordination ability toward Zn(II) ion in $CH_3CN:CH_2Cl_2$ solution. Moreover, upon naphthalene excitation photosensitized azobenzene isomerization takes place. To the best of our knowledge, this represents the first example of a dendrimer containing photochromic, luminescent and metal coordinating units.

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Keywords: *photophysics; azobenzene; metal complex; energy transfer; photoisomerization;*

Molecular devices and machines – III

O-208

A HYBRID DONOR-ACCEPTOR1-ACCEPTOR2 TRIAD BASED ON DIFFERENT ELECTRON ACCEPTING FULLERENES

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Donor-acceptor (D-A) systems have been extensively studied in order to understand the electron transfer (E.T.) process that takes place in the photosynthesis of plants.[1] The mechanism of this process is based on an unidirectional flow of electrons to generate a long-lived charge separation state, thus, the existence of a redox gradient between different fragments of the molecule, is an important issue to be addressed. Fullerenes and their derivatives have been used as electron acceptor compounds of these artificial models due to their electronic characteristics, providing an accelerate charge separation and decelerate charge recombination in the charge separation state.[2]

A great variety of dyads, triads and tetrads containing one fullerene unit have been reported, although the preparation of related systems bearing different fullerenes units have been explored in a lesser extent.[3]

Considering the unique properties of fullerenes and porphyrins, here we report the design and preparation of a new donor-acceptor$_1$-acceptor$_2$ (D-A$_1$-A$_2$) triad formed by Zn-porphyrin as electron donor and C_{60}/C_{70} fullerene dimer as electron acceptor fragment.[4]

The new triad displays an electron gradient due to the two different fullerene fragments present in the molecule. Photophysical studies reveal the existence of two processes of electron transfer. This triad represent one of rare case in which the E.T. goes from a primary electron acceptor (C_{60}) to a secondary electron acceptor (C_{70}) affording the radical ion par and the corresponding charge separation state.

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Keywords: *Fullerenes; Electron transfer;*

Nanoscale particles, cages, sheets and tubes – II

O-340

SUPRAMOLECULAR CHEMISTRY WITH CARBON NANOSTRUCTURES

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Among the wide range of novel nanometer scale structures available, single-wall carbon nanotubes (SWNT) and multi-wall carbon nanotubes (MWNT) and more recently, graphene, stand as unique materials for fundamental research and potential applications. However, manipulation and processing of NTs has been difficult because of their intractability and insolubility in most common solvents. Considerable effort has therefore been devoted to the chemical modification of NTs and graphene, which might pave the way to many useful applications.

Our group has been involved in the organic functionalization of various types of nanocarbons, including carbon nanotubes, nanohorns, fullerenes, graphene and nanoonions. During this talk, we will report on the most recent advances in our group, which have led to several interesting applications in many fields. For instance, functionalized carbon nanotubes stimulate neuronal communication or can serve as carriers for innovative drug delivery systems. Especially the use of carbon nanotubes as active substrates for neuronal growth has given so far very exciting results. Not only nanotubes are compatible with neurons, but especially they play a very interesting role in interneuron communication. Improved synaptic plasticity is just one example.

On the other hand, carbon nanostructures are ideal supports for catalysts useful in water splitting devices. Low overpotentials and high turnover numbers can be achieved using carbon nanostructures as active supports.

Keywords: *Carbon Nanotubes; Graphene; Supramolecular Chemistry; Water Splitting;*

Nanoscale particles, cages, sheets and tubes – II

O-341

FABRICATION, CHARACTERISATION, AND HEALTH CARE APPLICATIONS OF CARBOHYDRATE-CARBON HYBRID NANOMATERIALS

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Diamond and graphite are two allotropes of carbon with interesting, but completely differing chemical and mechanical properties. In diamond, the carbon atoms form a tetrahedral lattice, whereas in graphite they build up layers of sheets with the atoms in honeycomb arrangements. Their nanoscale structures, namely nano diamond (ND) and graphene sheets (GS), share a promising feature: low cytotoxicity.[1, 2] Therefore, functional ND- und GS-materials will become valuable tools for future health care applications.

We functionalised ND and GS covalently, using carbohydrates as biological recognition unit to yield gylco-ND[3] and glyco-GS, respectively. Glycoconjugates are ubiquitous biological structures, which serve as recognition site in many different cellular health- and disease-related processes.[4] Carbohydrate-carbon hybrids are thus benign biologically active nanoscale materials with a large potential in health care applications.

They can be applied for the quick, straightforward and efficient removal of pathogens from water samples[3] and further urgent health care issues.

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Keywords: *Nanoparticles; Glycoconjugates; Carbohydrates; Carbon; Biological activity;*

Nanoscale particles, cages, sheets and tubes – II

O-342

SYNTHESIS OF STAPLED PI-CONJUGATED HELICAL SCAFFOLDS. A BOTTOM-UP APPROACH TO CHIRAL CARBON NANOCOILS

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Carbon nanocoils (CNCs) are carbon allotropes with tubular diameters down to 20 nm. CNCs have been used to generate magnetic fields emulating the behaviour of a solenoid and they have shown pseudoelastic properties allowing elongations up to 42%. In a broad sense, [*n*]-helicenes and *o*-phenylenes can be considered CNCs but they have extremely rigid backbones in the axial direction and densely packed *pi*-systems. Hence, the expected electron transport (ET) through the helical backbone could be hindered by ET through the *p*-stacked rings. On the other hand, conformationally flexible *o*-phenylene-ethynylene oligomers (*o*-PEOs) can adopt helical arrangements by means of supramolecular interactions. The *covalent stapling* of conformationally dynamic *o*-PEOs would lead to the corresponding less tight CNCs. Here, we report on the synthesis and chiroptical properties of the smallest flexible member of CNCs family able to retain their striking properties.

Firstly, we screened some hydroxylated *o*-PEOs with different diacids and nanocoils were obtained in good yields. Using a chiral *l*-tartaric acid, an intramolecular central-to-helix chirality transfer was revealed by CD spectroscopy. However, *mono*-stapled compounds were too flexible and underwent racemization at room temperature. To increase the stiffness, we synthesized *bis-stapled* nanocoils and alkene methatesis was used to obtain asymmetrically *stapled* compounds. Computer models and CD measurements agreed that *meta*- and *para*- substituted compounds have *P* and *M* helical configuration respectively. DFT calculations also revealed that elongations up to 2 A (55% longer) were accessible with low energetic requirements (<3 Kcal mol^{-1}). An inspection of the HOMO-LUMO gaps during the stretching suggested that the *p*-stacking stabilisation was not present when the two final benzene rings were separated 0.75 A. In that case, the ET along the backbone would be favoured over the axial through-space ET emulating the behaviour of a solenoid.

Keywords: *helical structures; chirality; electron transport;*

Nanoscale particles, cages, sheets and tubes – II

O-343

ELECTROACTIVE CARBON-NANOFORMS: FUNCTIONALIZATION AND PROPERTIES

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Carbon-based materials such as fullerenes, carbon nanotubes or graphene, play a major role in today's science and technology. In particular, carbon nanotubes and more recently graphene offer promising opportunities for electronic devices and chemical sensors due to its striking mechanical, optical and electrical properties.

The development of functional structures, between different electroactive units and the previously mentioned carbon-nanoforms, able to transform sunlight into electrical or chemical energy are important features for the fabrication of innovative optoelectronic devices.

In this regard, the remarkable gain of aromaticity and planarity that π-extended TTF (exTTF) derivatives reveals upon oxidation renders them an interesting donor unit that has been extensively used in the preparation of different donor-acceptor ensembles. In the same way, heptamethine cyanine derivatives have been used for the preparation of donor-acceptor dyads considering fullerenes as electron acceptor fragments. On the other hand, interfacing strong electron-acceptors with different carbon-nanoform has been scarcely explored and, in this sense, tetracyanoanthraquinodimethane derivatives (TCAQ) are suitable electron-acceptor systems that have been investigated with respect to their charge-transfer efficiency to conjugated polymers and fullerenes.

However, for pursuing the practical applications of these carbon nanostructures, one major drawback is their difficult processability and/or dispersability which decrease the overall yields of usable material and interfere with most of the desired properties. A fair amount of work focuses on their non-covalent and the covalent functionalization as a means to overcome the obstacles of low solubility. While the supramolecular modification depends on interactions affected by multiple parameters (concentration, solvent,..), the covalente functionalization improves the stability of the nanoconjugates making them suitable for practical applications.

In this contribution, we will present different covalent approaches towards the formation of nanohybrids based on carbon nanotubes or graphene and different electron-donor (exTTF, cyanines) and electron-acceptor (TCAQ) moieties. The detailed characterization of these nanostructures will be discussed.

Keywords: *Nanotubes; Graphene; Donor-acceptor systems; Electron transfer;*

Nanoscale particles, cages, sheets and tubes – III

O-344

CHEMICAL FUNCTIONALIZATION OF SYNTHETIC CARBON ALLOTROPES

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Chemical functionalization of new C-allotropes is of fundamental interest and opens the door to unprecedented materials applications. In principle, the physical and chemical properties of fullerenes, carbon nanotubes (CNTs) and graphene are related to each other, although their levels of development vary considerably. In order to efficiently explore the reactivity of the less developed CNTs and especially that of graphene it is our goal to provide a unifying approach for the chemistry of all three new carbon allotropes. The fullerenes present the first family of synthetic carbon allotropes. Since their availability in macroscopic quantities numerous investigations with respect to their physical characterization and chemical functionalization have been carried out. CNTs - the second new family of C-allotropes – exhibit at least the same potential for unprecedented applications. Their chemistry, however, is much less developed. Although many protocols for covalent and non-covalent CNT functionalization have been published there are still many fundamental problems to be solved. This includes *inter alia* the highly selective functionalization of metallic- or semiconducting SWNTs, the high throughput isolation of SWNTs with single helicity, the development of general concepts allowing for tunable doping of individualized tubes with single helicity or least defined transport characteristics (metallic – semiconductive). Finally, the youngest representative in the list of new C-allotropes is graphene and the exploration of its chemistry has just begun to start. So far only investigation on the functionalization of defect rich graphene oxide (GO) but not intact graphene itself have been published. Compared to the various flavours of CNTs (broad variation of helicities, single walled, multi walled) graphene is a much more uniform material. This will facilitate the development of its chemistry considerably. We will present a series of new results of covalent and non-covalent functionalizations of fullerenes, carbon nanotubes and graphene.

Keywords: *graphene; fullerene; carbon nanotube; synthetic carbon allotrope;*

Nanoscale particles, cages, sheets and tubes – III

O-345

SILICON NANOCRYSTALS: WHY DO SOME EXHIBIT SIZE DEPENDENT PHOTOLUMINESCENCE WHILE OTHERS SIMPLY HAVE THE BLUES?

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Silicon nanocrystals (SiNCs) offer many benefits over prototypical CdSe quantum dots including biocompatibility. Adding to their appeal, SiNCs are also compatible with standard electronics and communications platforms, some exhibit size dependent photoluminescence and evidence to date suggests stabilizing surface groups are not labile. Numerous innovative solution-, gas-, and solid-phase methods have been developed to realize size-controlled SiNC synthesis. All procedures afford SiNCs that appear seemingly identical. However, based upon SiNC optical response it is clear they are not. SiNCs prepared using high-temperature methods routinely exhibit photoluminescence agreeing with the effective mass approximation. SiNCs prepared via solution methods exhibit blue emission that is independent of particle size. Despite many creative proposals, a concrete explanation for this difference has eluded the nanomaterials community for no less than a decade. This apparent dichotomy brings into question our understanding of SiNC properties and potentially limits the full scope their applications. This presentation will introduce SiNCs and many of the standard literature procedures used for their preparation. Focus will then shift to oxide-embedded and surface functionalized freestanding SiNCs prepared using procedures developed in the Veinot Laboratory and our deermination of the origin of the blue emission noted above. A detailed comparison of blue-emitting SiNCs synthesized by the Kauzlarich (UC Davis) and Tilley (Victoria University of Wellington) groups will also be described.

Keywords: *nanoparticles; quantum dots; silicon; semiconductors; fluoresence;*

Nanoscale particles, cages, sheets and tubes – III

O-346

FUNCTIONALIZED SILICON NANOCRYSTALS FOR PHOTOLUMINESCENCE BASED CHEMOSENSORS

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Physical properties of nanocrystalline silicon are substantially different as compared to crystalline silicon. One of the most striking is bright visible photoluminescence observed at room temperature. In the presence of chemical species photoluminescence changes and this behavior is employed in sensors of chemical compounds. Porous silicon is a nanocrystalline silicon based material with complex morphology especially useful for detection of chemical species.

Photoluminescence detection of organic compounds with porous silicon sensors is based on photoluminescence quenching. The magnitude of this quenching depends on both the concentration and quenching strength of analyte. The role of principal mechanisms of photoluminescence quenching in porous silicon - exciton dielectric quenching and capillary condensation effect – will be discussed and their manifestation in gas and liquid phase will be demonstrated. For applications in electronic noses or tongues an improvement of sensor selectivity response is needed. This task was achieved by functionalization of the porous silicon surface by molecules with molecular recognition properties. Examples of surface functionalization via several routes like oxidation (replacement of Si-H bonds with Si-O bonds), hydrosilylation with methyl-10-undecenoate and various beta-cyclodextrin derivatives (replacement of Si-H bonds with Si-C bonds) and electrodeposition of polymer films (polypyrrole) will be presented together with specific challenges in chemical manipulation of nanocrystalline silicon. Modification of photoluminescence sensor response due to surface functionalization will be presented and possible mechanisms behind modified sensors response will be discussed for various classes of organic molecules. Additional information about chemical nature of detected analytes can be obtained from measurements of photoluminescence decay time; advantages of simultaneous measurements of photoluminescence intensity and photoluminescence decay changes will be presented. Several topics connected with operation of porous silicon sensor in real applications will be addressed.

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Keywords: *silicon nanocrystals; porous silicon; chemosensors; photoluminescence; molecular recognition;*

Nanochemistry, nanotechnology and nanostructured materials – III

O-347

MULTIFUNCTIONAL SUPRAMOLECULAR ELECTRONICS

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Multifunctional materials are key in organic (opto)electronics. However, their practical use requires the optimization of the self-assembly of multimodular architectures at surfaces using non-conventional methods, their controlled manipulation and responsiveness to external stimuli, and the quantitative study of various physicochemical properties at distinct length-/time-scales. My lecture will review our recent results on:

- **(i)** Development of novel (post)processing methods to produce ordered supramolecular electroactive architectures.[1]
- **(ii)** Supramolecular scaffolding, based on H-bonding or metallo-ligand interactions, to control the position of functional units at surfaces.[2]
- **(iii)** Responsive interfaces like the realization of the first dynamer operating at surfaces visualized on the sub-nm scale by Scanning Tunneling Microscopy,[3] and prototypes of light-powered mechano-chemical switches. The bistable nature of the latter were exploited to develop optically-modulable nanoscopic and macroscopic junctions.[4]
- **(iv)** Scanning Probe Microscopies beyond imaging to explore electronics processes, like photovoltaic activities, in multicomponent architectures.[5] Further, the electrochemical local reduction of graphene oxide with and AFM tip followed by the C-AFM study of the electrical properties of the manipulated architecture will be presented,[6] towards blueprinting macromolecular electronics.[7]
- **(v)** Supramolecular approaches to organic electronics allow improvement of the performance of devices, e.g. through the tailoring of percolation pathways for charge transport in polycrystalline films for FETs,[8] bottom-up fabrication of asymmetric electrodes for ambipolar FETs,[9] and realization of bi-functional FET.[10]

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Keywords: *supramolecular electronics; self-assembly; nanochemistry;*

Nanochemistry, nanotechnology and nanostructured materials – III

O-348

MOLECULAR ELECTRONICS AT THE ULTIMATE LIMIT OF SINGLE MOLECULES INTERROGATED IN SOLID-STATE DEVICES

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One of the challenging goals of molecular electronics is to understand and master electronic devices at the single-molecule level. Based on recent progress employing three terminal solid-state devices[1-5] it is possible to interrogate a single molecule in a metal gap in great detail. The talk will focus on new insight into the physics and chemistry of such molecules in particular the influence of metal electrodes on the molecular energy spectrum[1], controlling molecular spin[2] and progress towards chemical preparation of single molecule devices in which the molecule/metal interface can be controlled with atomic precision.[3, 4] Finally, the talk will present very recent developments in the fabrication of molecular solid-state devices employing graphene as soft top-contacts [5].

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Keywords: *Single-molecule studies; Supramolecular chemistry; Molecular electronics; Nanotechnology;*

Nanochemistry, nanotechnology and nanostructured materials – III

O-349

CONTROLLED MOLECULAR SELF-ORGANIZATION FOR ELECTRONIC DEVICES WITH ENHANCED PERFORMANCE

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The realization of well-defined and ordered structures on the nanoscale is a main issue in nanoscience and nanotechnology, biotechnology and other related fields like plastic or organic electronics. Among the bottom-up approaches, to date, self-assembly of molecular systems (equilibrium aggregates) received a major attention. In spite of this, far from equilibrium conditions allow for the generation of a wider landscape of organized systems depending on the set of control parameters employed. Under an evolutionary vision of the structures, here some case studies show how it is possible to programme and control the nanoscale features of ordered super- or supra-molecular aggregates at wet interfaces by modulating static and/or dynamic parameters.[1, 2, 3] In this contest, speed is foreseen as a threshold factor for changing the aggregation mechanism along with the shape and degree of order of the structures as well as their size and defectivity. The second part of the presentation is dedicated to important properties of well-defined self-assembled/organized organic or hybrid structures in electronic devices. Also in collaboration with other groups, our efforts have been recently directed to develop molecular devices including single layer polymer transistors,[4] high-k smart nanodielectrics[5] and thin film bulk heterojunction solar cells[6] by employing new materials and deposition strategies including far-from-equilibrium processes. New strategies for the realization of 2D and 3D supramolecular ordered thin films for electronic devices with enhanced performance are highlighted.

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Keywords: *molecular electronics; self-assembly; self-organization; functional thin films; nanoscale order;*

Nanochemistry, nanotechnology and nanostructured materials – III

O-350

TRANSLATION, ROTATION AND LEVITATION OF MICRO AND NANO-OBJECTS BYBIPOLAR ELECTROCHEMISTRY

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Molecule and particle transport inside microdevices such as lab-on-chip or in biological systems is attracting an increasing attention. In this contribution, we propose new original concepts based on bipolar electrochemistry. When a conducing object is placed in an electric field, it gets polarized. Consequently, a potential difference appears between its two extremities that can be used to drive localized redox reactions. By using this phenomenon of bipolar electrochemistry, we were able to create in a straight forward way a large variety of asymmetric particles composed of different materials ranging from microfibers to the nanotubes. Some of these objects can be used as microswimmers. Indeed, the influence of an external magnetic field allows controlling the orientation of carbon microtubes functionalized with nickel. More recently, we could use the same substrates but modified with platinum to create micromotors in the presence of hydrogen peroxide.

The asymmetric reactivity that is induced by bipolar electrochemistry can also be used directly to generate motion of non-hybrid objects. Using this concept, it is possible to propel linearly metallic micro-dendrites using a deposition/dissolution mechanism. Electrogenerated hydrodynamics, either at both or one extremity of a conductive microobject can also be used for controlled propulsion. We recently demonstrated that this mechanism allows inducing rotations, translations and levitation. Bipolar electrochemistry is thus an original and competitive tool for generating motion at the micro- or sub-microscale, which opens new perspectives in micro- and nanosystem technologies.

Keywords: *Micromotors; Carbon nanotubes; bipolar electrochemistry; Swimmers;*

Nanochemistry, nanotechnology and nanostructured materials – IV

O-351

NANOCHEMISTRY AT SURFACES: FROM SINGLE MOLECULES TO COMPLEX ENSEMBLES

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Molecules are versatile entities conferring structural integrity and multi-faceted functional properties to both natural and artificial systems. By single-molecule positioning and supramolecular engineering at interfaces we can advance molecular science and nanochemistry. The insights thus gained affect various fields of application, including catalysis, sensing, light-harvesting, magnetic materials and organic electronics. The intriguing details of surface-confined molecular nanosystems, their special configuration, electronic characteristics, chemical reactivity and dynamics emerge from systematic scan-ning probe microscopy investigations, frequently employed in combination with a powerful range of space-averaging spectroscopy techniques and accurate computational modeling.

Here we explore molecular modules, steer their organization, and afford novel functions using well-defined surfaces as anchoring or construction platforms. The presented real-space observations visualize structural features with atomistic precision and reveal the molecular recognition and self-assembly phenomena mediating the expression of genuine nanoarchitectures. The multitechnique study of flexible species such as metalloporphyrins exemplifies the delicate interplay between conformational adaptation, electronic signature and axial ligation of adducts. We describe single-molecule conductance switching via prototropy within a tetrapyrrole macrocycle and stimulate rotational movements of rare-earth porphyrinato sandwich complexes created in vacuo. The devised bottom-up fabrication protocols implement biological and *de novo* synthesized building blocks and exploit error-corrective noncovalent bonding or metal-directed assembly. They yield distinct nanoarchitectures: supramolecular gratings, hierarchic structures, and metal-organic cyclic supramolecules, flexible chains and regular networks. Using porous nanomeshes we demonstrate tunable electron confinement, and follow the supramolecular dynamics of caged species. The developed strategy presents a rationale for the control of adaptive molecular species at interfaces and the design of highly organized molecular nanosystems with complex features and tunable functional properties.

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Nanochemistry, nanotechnology and nanostructured materials – IV

O-352

NANOPATTERNING BY MOLECULAR POLYGONS

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The self-assembly of shape-persistent molecules with flexible alkyl/alkoxy side chains provides an efficient approach towards two-dimensional supramolecular crystalline surface patterns at the solution/solid interface. *In-situ* scanning tunneling microscopy yields a submolecularly resolved insight into the adlayer structures and thus a conclusion on the driving forces for their formation. Of particular interest is how the nanoscale architectures depend on the symmetry and substitution pattern of the molecular building blocks. One approach towards tailored adlayers is based on the adsorption of shape-persistent arylene-alkynylene macrocycles at the interface of 1,2,4-trichlorobenzene and highly oriented pyrolytic graphite.[1] Recent work has focused on macrocycles involving dithiophene corner building blocks connected via linear phenylene-ethynylene-butadiynylene units that can be viewed as molecular polygons of distinct symmetry (i.e. triangles, squares, pentagons, and hexagons).[2] Concepts of discrete geometry are applied to design and describe such nanoscale surface patterns. The results gain insight into the 2D crystallization of nanoscale pentagons, binary mixtures of triangles and hexagons, and how large periodicities of >10 nm become accessible.

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Keywords: *self-assembled monolayers; scanning tunneling microscopy; solid/liquid-interface; shape-persistent macrocycles;*

Nanochemistry, nanotechnology and nanostructured materials – IV

O-353

SELF-ASSEMBLY OF CHARGED NANOPARTICLES AT FLUID INTERFACES

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Inspired by nature, self-assembly phenomena are currently the subject of intensive studies in modern science. Autonomous organization of individual elements into complex structures is increasingly considered the best “bottom-up” approach to fabricating novel materials.

Herein we present self-assembly of charged nanoparticles (NPs) into hexagonally close-packed lattices at fluid interfaces.[1] We employ gold NPs covered with a mixture of ionic (charged) and hydrophobic ligands. At a certain ligand ratio, the NPs display a property to absorb spontaneously at fluid interfaces producing monolayers. We found that such self-assembled NPs exhibit Janus-type amphiphilic structure and possess well defined and constant charge. At oil-water interface, the NPs autonomously form hexagonally packed lattices as a result of a fine balance between repulsive electrostatic and attractive hydrophobic forces. In turn, at air-water interface, the NPs arrange into sparse monolayers which then can be readily compressed to give dense films by using Langmuir-Blodgett technique. The NP monolayers squeezed into such films can be used for coating of various materials.

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Keywords: *Nanoparticles; Self-assembly; Interfaces; Monolayers;*

Nanochemistry, nanotechnology and nanostructured materials – IV

O-354

CHEMISTRY IN NANO-SCALE OPTICAL CAVITIES

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Chemistry is normally controlled by reaction conditions such as the type of solvent, the concentration of reactants, and temperature. The reaction barrier can be lowered by the use of catalysts or bypassed by the absorption of thermal or photonic energy by one of the reactants. In this contribution we explore the notion that one can influence a chemical reaction via a very different path: by the strong coupling of molecules and photons to form new, hybrid light/molecule states.

Strong coupling phenomena are most familiar to chemists in the exchange of electron density between atomic orbitals to form molecular bonding and anti-bonding orbitals. Physical chemists are likewise familiar with the strong coupling of resonant transitions of molecules in aggregates (exchange of excitation energy) generating hybrid states of higher and lower energy, sometimes labelled H- and J-aggregate bands respectively depending on their geometry. Less intuitive is that strong coupling can also be found at the level of molecules exchanging photons with a resonant optical cavity, forming hybrid light/matter states (or cavity polaritons).[1, 2]

We will present studies of molecular systems inside nano-scale optical cavities formed by two metallic mirrors, demonstrating clearly that molecular reactivity is modified by strong interaction with cavity optical fields.

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Keywords: *Nanostructures; Reaction mechanisms; Photophysics; Energy transfer; Photochromism;*

Nanochemistry, nanotechnology and nanostructured materials – IV

O-355

EXPLOITING P CHEMISTRY FOR GAP FINE-TUNING AND COORDINATION-DRIVEN ASSEMBLY OF POLYCYCLIC AROMATIC HYDROCARBONS

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Among the different families of π-conjugated systems, polycyclic aromatic hydrocarbons (PAHs) proved to have a great potential in the field of molecular electronics.[1] Due to the high flexibility of organic synthesis, many strategies can be considered to tune the bandgap and the supramolecular organization of PAHs. A fruitful approach involves the incorporation of heteroatoms (N, S, B) within the C-sp^2 frameworks.[2] Here, we report that this appealing strategy can be extended to P-modified PAHs. We report on the synthesis, structural and optical properties of the first family of P-containing PAHs, namely dibenzophosphapentaphenes.[3] In addition to the synthetic challenge that represented the insertion of a reactive σ^3,λ^3-P-moiety in a PAH backbone, we show that P-chemistry allows an unprecedented molecular engineering of both the bandgap and the supramolecular organization of PAH. In particular, P-chemistry allows readily preparing, from one single precursor, a new family of PAHs with tunable optical (absorption/emission) and redox properties. Furthermore, the coordination ability of P-ligands, illustrated with the coordination to Au^I, allows for unprecedented coordination-driven assembly of PAHs. This molecular engineering strategy based on organophosphorus chemistry shows the potential of introducing P into planar p-extended frameworks.

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Keywords: *aromatics; graphene; phosphorus; coordination;*

Nanochemistry, nanotechnology and nanostructured materials – IV

O-356

RATIONAL SYNTHESIS OF 2D POLYMERS

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The present interest in graphene, a naturally occurring two-dimensional polymer, makes clear that there is no synthetic method available that would allow accessing a covalently bonded molecular sheet with internal periodicity and a thickness of one monomer unit only in a non-thermolytic rational way.[1] After a brief historic overview, the concepts will be presented which are presently being pursued in the authors' laboratory. They rest upon carefully designed monomers, interfacial as well as single crystalline ordering, and both metal-complexation[2] and light-induced topochemical polymerizations.[3] The lecture introduces the first case of a 2D polymer with internal periodicity composed of areal repeat units. This is an extension of Staudinger's polymerization concept but in two dimensions.

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Keywords: *periodic network; areal repeat units; molecular sheets; topochemical reaction;*

Nanoscale particles, cages, sheets and tubes – IV

O-467

CONTROLLING THE PHOTOEMISSION OF QUANTUM DOTS BY METAL AND REDOX ACTIVE COMPLEXES

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We have developed the use of polyethylene glycol (PEG)-based modular multifunctional ligands to functionalize a variety of inorganic nanoparticles and transfer them to buffer media. We have also designed approaches to conjugate various biomolecules to CdSe-ZnS core-shell semiconductor quantum dots (QDs), Au nanoparticles (AuNPs) and magnetic nanocrystals.

In this presentation, we investigate the charge transfer interactions between luminescent QDs and metal or redox-active complexes. In one system we use ZnS-overcoated CdSe QDs surface-capped with poly(ethylene glycol)-appended dihydrolipoic acid (DHLA-PEG) covalently coupled to dopamine-isothiocyanate. For this system in particular, we found that in addition to the effects of conjugate valence the QD PL quenching efficiency can be (**a**) substantially increased in alkaline buffers compared to acidic conditions, and (**b**) strongly affected by changes in the buffer pH and the presence (or absence) of oxygen. These produce valence-and pH-dependent PL quenching combined with shortening of the exciton lifetime, while altering the recombination kinetics of both the electron and hole of photoexcited QDs.

We will provide the experimental details, discuss steady-state and time-resolved data, and provide results from transient absorption measurements where a simultaneous change in the electron and hole intraband relaxation dynamics has been measured when the pH was switched from acidic to alkaline.

Keywords: *quantum dots; fluorescence; charge transfer; quenching; pH;*

Nanoscale particles, cages, sheets and tubes – IV

O-468

LUMINESCENT QUANTUM-DOT/POLYMER/GOLD NANOPARTICLE ASSEMBLIES

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Metal-semiconductor hybrid nanostructures have attracted increasing attention, with many potential applications in functional optoelectronic devices, sensors, imaging, photocatalyst, etc. Here we present the preparation of hierarchical structures by self-assembling amphiphilic block copolymer chains, using the micelle cores as nanoreactors to prepare CdS quantum dots (QDs), and the thiol chain-end groups in the polymer shell to anchor gold nanoparticles (GNPs). The GNP surface plasmons create locally-enhanced electromagnetic fields in the vicinity of the metal surface that can be used to increase the emission of QDs in close proximity to the metallic nanoparticles.

We synthesized a symmetric amphiphilic block copolymer, composed by two long polystyrene (PS) inner blocks and two short poly(acrylic acid) (PAA) outer blocks connected by a central trithiocarbonate (TTC) group, using a sequential RAFT controlled polymerization technique. In 1,4-dioxane, the block copolymer chains self-assemble to form spherical micelles with a PAA core and a flower-like PS shell. The cores were then used as nanoreactors to prepare cadmium sulfide (CdS) semiconductor nanoparticles. We transformed the micelle shell TTC groups into thiol groups, which were then used to anchor GNPs. The size of the PS blocks is used to control the GNP-QD distance, in order to obtain a strong GNP-QD interaction, while avoiding the possibility of luminescence quenching occurring at close contact. Using different ratios of GNP:QD we observed an increase in the QDM luminescence intensity for higher gold concentrations, after a correction for the GNPs inner filter effect. The GNP-decorated, polymer coated QDs provide an excellent platform for tunable photonic and biolabeling materials.

Keywords: *hybrid nanostructures; RAFT polymerization; quantum dots; metal nanoparticles; luminescence;*

Nanoscale particles, cages, sheets and tubes – IV

O-469

LUMINESCENT CORE-SHELL NANOPARTICLES FOR IMAGING AND SENSING

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Luminescence finds important applications in many different fields and the development of new emissive components for real-time and space-resolved detection is still an issue. Nanosciences have opened up many new possibilities to this aim allowing the creation of promising platforms for the implementation of new luminescent targeting materials.

We recently proposed a new versatile synthetic approach to obtain very mono-disperse, water soluble core-shell nanoparticles (NPs) presenting a silica core (10 nm of diameter) and an organic shell (7 nm thick) that can host organic dyes, even of different nature. These NPs are brightly luminescent, photostable, and their spectral profile can be easily tuned with a proper choice of the doping dyes.[1] The NPs can be obtained with a one pot approach even with modified terminal groups on the organic shell, this introduces a large chemical versatility that allows coupling with suitable species (e.g biomolecules) for specific target. This feature, together with the biocompatibility of the materials, and the use of dyes absorbing and emitting in the Near Infrared Region (NIR) (a transparent region for biological tissues) make these species particularly suitable for application in *in-vivo* and *in-vitro* imaging. Examples will be discussed together with other designs of the same platform for multiplexed analysis and nanosensor applications.[2]

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Keywords: *nanoparticles; luminescence; imaging agents;*

Nanoscale particles, cages, sheets and tubes – IV

O-470

SUPERPARAMAGNETIC CORE-SHELL NANOPARTICLES AS COLLOIDAL SUPPORT FOR PEPTIDE SYNTHESIS

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A fast and facile microwave assisted synthesis of core-shell nanoparticles is presented, resulting in monodispers colloids with magnetite cores[1] coated by functionalized silica shells, which have been applied as solid supports to facilitate peptide synthesis.

Solid-phase supported peptide synthesis (SPPS), introduced by Merrifield in 1963, has revolutionized molecular biochemistry, pharmacology, biomedicine and biophysics, but also enabled means of combinatorial chemistry. Since the initial work of Merrifield, the applied solid supports have not been dramatically changed. Lightly cross-linked polystyrene resins with 1% divinylbenzene are the most used solid supports for peptide synthesis. Using nanoparticles as solid supports would overcome several difficulties, inherent to the micro gel supports as direct accessibility of the functionalities on permanent surfaces are provided and diffusion limitations of reactions in micro gel particles will be overcome.

Here we present our study applying monodispers core-shell nanoparticles as a solid support for SPPS.[2] Superparamagnetic magnetite monodomain nanoparticles are coated in a microwave assisted Stöber-process with a functional silica shell carrying amino-groups that are used to introduce linkers required for SPPS. Average particle sizes of 70 nm allow 'quasi homogeneous' synthesis in solution. An external magnetic field is used to separate the solid support reversible and effectively from the reaction mixture, ensuring ease of purification. Magnetic sedimentation of the particles means ease of purification and core shell structure effectively improves resistance of the magnetite core particles against strong acids and bases.

Several peptides were synthesized, using sequential assembly of Fmoc-protected α-amino acid derivatives, implementing colloidal supports to standard SPPS procedures. As model a tetrapeptide with a sequence Phe-Lys-Leu-Gly was synthesized. The peptide could be conveniently isolated from the cleavage solution with yields of ~70% and analysis of the resulting crude peptide exhibits remarkable product purity of ca. 95%.

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Keywords: *Nanoparticles; Solid-phase synthesis; Microwave chemistry; Magnetic properties;*

Nanoscale particles, cages, sheets and tubes – V

O-471

LUMINESCENT NANOSWITCHES

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The goal of our research program is the identification of viable strategies to switch luminescence under optical control. In this context, we are developing two families of nanostructured constructs with photoswitchable luminescence. One of them is based on the ability of amphiphilic polymers to trap fluorescent and switchable components in their hydrophobic interior. The other relies of the passivation of luminescent quantum dots with switchable polymer ligands. In both instances, optical stimulations can be exploited to control the state of the switchable components and in turn regulate the emission of the luminescent components. The resulting photoswitchable luminescent constructs can be operated in aqueous environments, can cross the membrane of living cells and are not cytotoxic. Furthermore, their unique photoswitchable character offers the opportunity to record images with subdiffraction resolution as well as to monitor the diffusion of species. As a result, our luminescent nanoswitches might evolve into valuable analytical tools for a diversity of biomedical applications.

Keywords: *Luminescence; Photochromism; Photocages; Polymer Micelles; Quantum Dots;*

Nanoscale particles, cages, sheets and tubes – V

O-472

CONJUGATED POLYMER NANOPARTICLES FOR CELL LABELLING, IMAGING AND DRUG DELIVERY

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Nanoparticles based on conjugated polymers are emerging as a new class of luminescent nanoparticles. These nanoparticles have many potential applications including imaging agents, biosensors, and photonics owing to their high quantum yields, high molar absorptivity, photo stability and easy synthesis. The recent cell assay studies have also showed that these nanoparticles were not cytotoxic.[4] Moreover, conjugated polymer nanoparticles can be modified easily to deliver therapeutic agents such as cancer drugs, genetic materials (e.g. RNA, siRNA) and biomolecules to the desired targets.

Here, we present the resent studies in our lab involving the synthesis and applications of nanoparticles using various conjugated polymers which emit blue, green, yellow and red. In order to obtain shape-persistent and stable nanoparticles, a novel method was developed in which the nanoparticles were prepared either via Cu-catalyzed or cucurbit[6]uril (CB6)-catalyzed click reactions between azide groups containing hydrophobic fluorene-based conjugated polymers and a hydrophilic diaminodialkyne containing cross-linker. Through the click reaction, not only does the cross-linking confer stability, but it also introduces functional groups, such as triazoles and amines, to the nanoparticles. TEM images of the nanoparticles also showed that they display very interesting morphologies. Incorporation of hydrophilic functional groups to the hydrophobic conjugated polymers resulted in a distinct phase separation, producing Janus-like or patchy particles.

We have also demonstrated the applications of these conjugated polymer nanoparticles in the *in vitro* cell labelling and imaging of a number of different cell lines (e.g. multipotent mesenchymal stem cells, RAW264.7 and Huh7). The conjugated polymer nanoparticles have also been loaded with various anti-cancer drugs and the delivery of drugs has been investigated *in vitro* in the cancer cell lines. The cell assay studies show that the drug loaded nanoparticles are up-taken by the cells efficiently and more effective comparing to the free-drugs in killing the cancer cells.

Keywords: *Nanoparticles; Nanotechnology; Polymers; drug delivery; fluorescent nanoparticles;*

Nanoscale particles, cages, sheets and tubes – V

O-473

PHOTOACTIVATED NANOASSEMBLIES WITH BIMODAL PHOTODYNAMIC ACTION

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[3] *Charles University of Prague, Faculty of Science, Prague, Czech Republic*

Multimodal therapies aim to exploit either additive or synergistic effects arising from the generation of multiple active species in the same region of space with the final goal to maximize the therapeutic effectiveness.[1] Light is a powerful mean for the non invasive introduction of therapeutic agents in a desired bio-environment, mimicking an "optical syringe" with an exquisite control of site, timing and dosage of the released species, factors playing key roles in determining a positive therapeutic outcome.[2] Singlet oxygen ($^1O_2$) and nitric oxide (NO) play a key role in anticancer cancer and antibacterial therapy. Typical for both species is their easy diffusion in the cellular environment due to their very small size compared to some conventional drugs, lack of charge and lipophilic character. Moreover, common to both $^1O_2$ and the NO radical is their potential to attack biological substrates of different nature representing multitarget therapeutic agents and avoiding Multiple Drug Resistance problems encountered with several conventional drugs often target-specific. Finally since the NO release from the NO photodonors is independent from O_2 availability it can potentially very well complement the $^1O_2$ effects at the onset of hypoxic conditions. In this contribution we report the design and fabrication of biocompatible cyclodextrin-based nanoparticles and nanogels able to combine the simultaneous delivery of $^1O_2$ and NO with imaging capacity under excitation with visible light. In this view, these multifunctional nanoconstructs represent appealing candidates for applications in biomedical research.

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Keywords: *Light; therapy; nanoparticles; singet oxygen; nitric oxide;*

Nanoscale particles, cages, sheets and tubes – VI

O-474

UNEXPECTED ELECTROCATALYTIC PROPERTIES OF MONOLAYER PROTECTED GOLD CLUSTERS

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The high catalytic activity of nanoscopic gold surfaces initially surprised the scientific community but is now well known and has given rise to a burgeoning new field of research. Most work in this area has been carried out on clean gold clusters in the 1 to 5 nm range deposited on oxide supports such as titania, while practically no attention has been paid to ligand-protected gold nanoparticles, so called monolayer protected clusters (MPCs), since these are generally assumed to be catalytically inactive due to the presence of the passivating ligand shell. Here we report that MPCs protected by mercaptoalkyl ethyleneglycol ligands exhibit unexpected catalytic activity for the electrochemical reduction of protons to adsorbed molecular hydrogen. There is no detectable equivalent reaction on macroscopic gold surfaces, where hydrogen evolution occurs at significantly more negative potentials and without a preceding adsorptive step. Similarly, under potential deposition (UPD) of certain metals including Cd can be observed on the same type of MPC. It is argued that the clusters exhibit highly reactive unsaturated surface sites (atoms) that are not covered by the thiol ligand and are therefore accessible to react with small molecules and ions capable of penetrating the ligand shell. The number of these active sites has been quantified for cluster sizes of 3 and 15 nm. Electrical contact is established by the spontaneous adsorption of the clusters to a hanging Hg drop electrode. The contact to the Hg electrode is very robust and does not lead to the formation of amalgams even after many hours of cycling the potential. We believe that, apart from its fundamental interest, this very unusual electrocatalytic behaviour of ligand-protected gold nanoparticles reported here, may lead to new strategies for the design of catalysts for the selective reduction or hydrogenation of small molecules.

Nanoscale particles, cages, sheets and tubes – VI

O-475

NANOSTRUCTURED MATERIALS BY COVALENT SELF-ASSEMBLY

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We recently reported a novel approach to the synthesis of polymer nanocapsules, which offer a wide range of applications including drug delivery, using a rigid, disk-shaped monomer with multiple polymerizable groups at the periphery. Without needs for any pre-organized structures or templates, and core-removal, this method directly produces polymer nanocapsules with a highly stable structure and relatively narrow size distribution. The polymer shell made of cucurbituril, a hollowed-out pumpkin-shaped host molecule, allows tailoring of its surface properties by host-guest interactions. The easy synthesis and unique ability to tailor surface properties in a noncovalent manner make the polymer capsule potentially useful in many applications including targeted drug delivery. This approach has been extended to include a wide range of cores, linkers and polymerization methods to synthesize new nanocapsules with interesting physical and chemical properties, and application perspectives. This strategy can also be extended to synthesize other nanostructured materials including two-dimensional polymers with single monomer thickness. The details of the work will be presented.

Keywords: *self-assembly; nanostructures; polymers;*

Nanoscale particles, cages, sheets and tubes – VI

O-476

STEP BY STEP GROWTH OF GOLD NANOPARTICLES AND GOLD NANORODS AND THEIR BEHAVIOR IN CATALYSIS

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Catalytic site effects for colloidal nanoparticles at the transition point from heterogeneous to homogenous catalysis are in the focus of on-going research because of the tunability of size, shape, stabilizer, and material. Thus, these systems have been studied intensively in oxidative and reductive catalysis.[1, 2]

A standard system for the investigation of reductive catalytic reactions in aqueous media is the reduction of 4-nitrophenol to 4-aminophenol with sodium borohydride. The monitoring can be done using UV-Vis spectroscopy following the intensities at 400 nm. In our study, we have investigated the reduction catalysis using gold nanoparticles and nanorods synthesizes with the seeding growth method.[3, 4] Different sizes of narrow size distributed gold nanoparticles and different length of gold nanorods, their reaction rates and the activation energies of the reactions were determined. The size parameters of the gold nanorods were measured by TEM, AFM, DLS and SAXS. The highest activity was found for particles with 13 nm diameter.[5] Furthermore, we have shown that longer gold nanorods have an higher catalytic activity in the tested systems.[6] These unexpected findings will be discussed systematically.

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Keywords: *Gold; Heterogeneous catalysis; Nanoparticles; Nanostructures;*

Nanoscale particles, cages, sheets and tubes – VI

O-477

INTRINSICALLY CHIRAL THIOLATE-PROTECTED GOLD CLUSTERS: ENANTIOSEPARATION, CHIROPTICAL PROPERTIES AND FLEXIBILITY OF AU38

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Bestowing chirality to metal surfaces and nanoparticles has become an intensive field of research. Such systems are promising candidates for enantioselective catalysis and for other applications in chiral technology in general.

Chirality in metal nanoparticles leads to optical activity, i.e. the differential absorption of left- and right-circularly polarized light.[1, 2] The origin of this optical activity is still debated, as several competing mechanisms may be responsible for it. Up to now optical activity was only observed for particles that are covered by chiral thiols. However, from X-ray structural analysis it became clear very recently that even particles covered by achiral thiols can be chiral due to the arrangement of the ligands in their surface.[3, 4] The importance of this type of surface chirality for the observed optical activity could not be studied yet, because all the samples prepared up to now were racemic and were therefore not optically active.

In our contribution we demonstrate for the first time the separation of a gold particle or cluster, $Au_{38}(SCH2CH2Ph)_{24}$, covered by achiral thiols into its enantiomers using chiral HPLC.[5] The optical activity of the separated enantiomers is very strong and the observed anisotropy factors are the largest ever observed for gold nanoclusters. This demonstrates the importance of the surface structure of the particles for their optical activity.

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Keywords: *chirality; optical activity; gold nanoparticles; enantioseparation;*

Organometallic Chemistry, catalysis, new frontiers – I

O-072

POLYFUNCTIONAL ORGANOMETALLICS AS KEY INTERMEDIATES IN ORGANIC SYNTHESIS

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Polyfunctional zinc, magnesium, and lithium organometallics are key organometallic intermediates in organic synthesis and new advances in the preparation and synthetic use of these organometallics will be presented. Thus, a stereoselective preparation of cyclohexyl-lithiums and related reagents by using a novel iodine-lithium exchange will be shown. The configurational stability of secondary cycloalkyl lithium, magnesium, and zinc reagents will be discussed as well as the stereochemistry (retention or inversion) of their reactions with various organic electrophiles. By using sterically hindered magnesium amides, selective directed metalations of functionalized aromatics and heterocycles will be performed. Also the preparation of air-stable zinc aryl and heteroaryl zinc pivalates will be shown. Applications of these new reagents in palladium-catalyzed cross-couplings as well as in the construction of heterocyclic scaffolds will be reported.

Keywords: *Cross-coupling; Lithium; Magnesium; Palladium; Zinc;*

Organometallic Chemistry, catalysis, new frontiers – I

O-073

NEW METHODS OF ENANTIOSELECTIVE SYNTHESIS WITH SCANDIUM AND SILANEDIOL CATALYSIS

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Our goal is to develop catalysts and synthetic methodology that mini-mize the use of reagents and or-ganic sol-vents, increase efficiency, and approach 100% selec-tivity. We are investigating the activity and selectivity of various catalyst systems for carbon-carbon bond-forming reactions and the enantioselective synthesis of complex molecules such as oxindoles and spirooxindoles will be presented. Catalysts discussed will include scandium- and indium-based chiral Lewis acids, Bronsted acids, and silanediols as a new class of hydrogen-bonding catalysts. Of particular interest, a catalytic asymmetric [3+2] annulation reaction of allylsilanes with bidentate electrophiles will be presented to generate carbocycles and heterocycles. This lecture will also discuss mechanism and molecular insights for catalyst activity and design.

Keywords: *Asymmetric catalysis; Asymmetric synthesis; Hydrogen bonds; Heterocycles; Silicon;*

Organometallic Chemistry, catalysis, new frontiers – I

O-074

CYCLOPENTADIENYL TITANIUM(IV) COMPLEXES WITH FLUOROUS PONYTAILS IMMOBILIZED ON CARBOSILANE DENDRIMERS VIA A TI-O BOND

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Recently we synthesized light[1] and heavy[2] fluorous cyclopentadienes with silyl substituents bearing up to three fluorous ponytails. Both monocyclopentadienyltrichlorotitanium and dicyclopentadienyldichlorotitanium (titanocene) complexes were prepared starting from the new ligands. We wondered, whether the monocyclopentadienyl complexes could be immobilized on a soluble polymeric support with low polydispersity, i.e. a carbosilane dendrimer. To provide comparison, reactions with nonfluorinated complexes were also carried out.

Dendritic polyols of the second and third generation 2G-OH_8, 2G-OH_{16}, and 3G-OH_{16} were prepared by hydroboration/oxidation of allyl terminated carbosilane dendrimers and used as supports for immobilization of cyclopentadienyltrichlorotitanium(IV) complexes via alcoholysis. Their reaction with $CpTiCl_3$ gave metallodendrimers

2G-$(OTiCpCl_2)_8$, 2G-$(OTiCpCl_2)_{16}$, and 3G-$(OTiCpCl_2)_{16}$, respectively, whereas the reaction of the dendrimers with

$CpSi^FTiCl_3$ ($CpSi^F = C_5H_4SiMe_2CH_2CH_2C_8F_{17}$) yielded peripherally fluorinated metallodendrimers 2G-$(OTiCpSi^FCl_2)_8$ and

3G-$(OTiCpSi^FCl_2)_{16}$. All metallodendrimers were characterized by multinuclear NMR spectroscopy and the proposed structure was further confirmed by comparison with model 1-propoxycomplexes.[3]

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Keywords: *Fluorinated ligands; Cyclopentadienyl ligands; Dendrimers; Silanes; Titanium;*

Organometallic Chemistry, catalysis, new frontiers – I

O-075

BIDENTATE LEWIS ACID CATALYSIS – A NEW ENTRY TO HIGHLY SUBSTITUTED NAPHTHALENES

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Multidentate interactions are the secret to nature's catalysis. Nonetheless, the application of these principles remains an extremely challenging endeavor. In organic synthesis the Lewis acid catalysis presents a very effective tool for a variety of different transformations. Although effort has been made towards bidentate Lewis catalysts still they react in a monodentate fashion.[1]

Recently, we were able to show the catalysis of the inverse electron-demand Diels-Alder (IEDDA) reaction of 1,2-diazines by a bidentate Lewis acid in a bidentate fashion.[2] The general principle is based on the following rational: The twofold coordination of the bidentate Lewis acid to the 1,2-diazine decreases the energy level of the LUMO facilitating the cycloaddition step. Consecutive elimination of N_2 generates the product and also liberates the catalyst.

This new concept of catalysis is furthermore combined with a novel one-pot synthesis of 1,2-diazino aromatics, developed in our group, to produce highly substituted naphthalenes in two steps from aromatic aldehydes. This strategy was applied for an efficient preparation of Naproxen.

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Keywords: *Lewis acids; Cycloaddition; Homogeneous catalysis; Heterocycles;*

Organometallic Chemistry, catalysis, new frontiers – II

O-076

ARTIFICIAL METALLOENZYMES BASED ON BIOTIN-AVIDIN TECHNOLOGY: RECENT ADVANCES AND CHALLENGES

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Artificial metalloenzymes result from incorporation of a organometallic moiety within a protein. We have been exploiting the potential of the biotin-avidin technology for the creation of artificial metalloenzymes. Thanks to the remarkable affinity of biotin for either avidin or streptavidin, covalent linking of a biotin anchor to a catalyst precursor ensures that, upon stoichiometric addition of (strept)avidin, the metal moiety is quantitatively incorporated within the host protein.

Such artificial metalloenzymes are optimized either by chemical (variation of the biotin-spacer-ligand moiety) or genetic (mutation of (strept)avidin) means. Such chemogenetic optimization schemes were applied to various organic transformations. The reaction implemented thus far include: **1**) The rhodium catalyzed hydrogenation of *N*-protected dehydroaminoacids (ee up to 95 %). **2**) The palladium catalyzed allylic alkylation (ee up to 95%). **3**) The ruthenium pianostool catalyzed transfer hydrogenation of prochiral ketones and imines (ee up to 97 %). 4) The vanadyl catalyzed oxidation of prochiral sulfides (ee up to 93 %). **5**) The osmium catalyzed dihydroxylation of olefins (ee up to 97 %). **6**) The ruthenium catalyzed oxidation of alcohol to ketones and the ruthenium catalyzed olefin metathesis.

Noteworthy features, reminiscent of homogeneous catalysis include: the straightforward access to both enantiomers of the product; broad substrate scope; organic solvent tolerance and reactions typical of homogeneous catalysis. Enzyme-like features include: genetic optimization; aqueous medium as the preferred solvent; Michaelis-Menten behaviour; single substrate derivatization. X-ray characterization of artificial metalloenzymes provide a fascinating insight into possible enantioselection mechanims involving a well defined second coordination sphere environment. Thus, such artificial metalloenzymes combine attractive features of both homogeneous and enzymatic kingdoms.

After presenting an overview of recent results for the above reactions, the last part of the talk will outline our current efforts on performing catalysis on crude cell extracts, thus paving the way towards directed evolution of artificial metalloenzymes.

Keywords: *Artificial metalloenzymes; Biotin-avidin technology; Enzyme design; enantioselective catalysis; bioinorganic chemistry;*

Organometallic Chemistry, catalysis, new frontiers – II

O-077

ALTERNATIVE METHODS FOR CARBONYLATION REACTIONS OF ALKENES AND ALKYNES

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Metal-catalyzed carbonylation reactions represent a very efficient and attractive synthetic method for carbonyl compounds.[1] Carbonylations of olefins belong to the most important industrially applied homogeneous catalytic transformations. Among them, alkoxycarbonylation, also called hydroesterification of olefins represents a very efficient method for the conversion of olefins, CO and alcohols to the corresponding esters.[2] On the other hand, selective carbonylations of tripple bonds can provide valuable intermediates for organic synthesis, such as unsaturated carboxylic acid derivatives.

Herein, we would like to present few novel methods for carbonylations of alkenes and alkynes. On the one hand, reactions based on use of non-gaseous CO-sources, such as formic acid derivatives, will be shown.[3] They are promising alternatives to the toxic and gaseous carbon monoxide.

Furthermore, the use of unusual, non-precious metals for carbonylations will be described. Recently, we have developed efficient iron-catalyzed mono- and diaminocarbonylations of alkynes.[4] Depending on the CO-pressure, either succinimides (10 bar) or cinamic amides (20 bar) can be obtained.

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Keywords: *homogeneous catalysis; carbonylation; Sustainable Chemistry;*

Organometallic Chemistry, catalysis, new frontiers – II

O-078

DESIGN AND CATALYTIC ACTIVITY OF NITROXIDE ORGANOCATALYSTS

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Nitroxides are intriguing compounds with many potential applications such as polymerization initiators, radical trapping reagents and catalysts for the oxidation of alcohols. Key to their catalytic reactivity is the integrity of the nitroxyl/oxoammonium functionality under the reaction conditions. However, this stability can normally only be insured by attaching two alkyl groups on either side of the nitroxide. Nitroxides bearing alfa hydrogen, although potentially more reactive catalysts undergo rapid decomposition to the corresponding catalytically inactive nitrones.

We have developed a new design concept to ensure the stability of nitroxides with alfa hydrogens. We will present the first C2-symmetric nitroxide prepared according to this concept. This compound is able to efficiently oxidize even highly sterically alcohols at low catalyst loadings (2 mol%). We will discuss the properties of these compounds and their potential applications in asymmetric catalysis.

Organometallic Chemistry, catalysis, new frontiers – III

O-079

WELL-DEFINED CATIONIC GALLIUM(III) COMPLEXES: A NEW TOOL IN ORGANIC SYNTHESIS

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Well-defined neutral and cationic gallium(III) halide complexes have been synthesized and evaluated in catalysis. Both the $(NHC)GaX_3/AgSbF_6$ catalytic mixture and isolated $(NHC)GaX_2^+$ species function as exquisite π-Lewis acids in typical GaX_3-catalyzed reactions. The cationic complexes are more active than GaX_3 and yet more resistant to hydrolysis, which allows lower catalytic loadings and faster reactions. Reactions that are not catalyzed by standard π-acids such as gold or platinum complexes are now possible with these new gallium species.

Keywords: *cycloisomerization; gallium; homogeneous catalysis; Lewis acids; N-heterocyclic carbenes;*

Organometallic Chemistry, catalysis, new frontiers – III

O-080

NEW RU(II) CATALYSTS FOR THE ASYMMETRIC REDUCTION OF KETONES.

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[1] *University of Warwick, Chemistry, Coventry, United Kingdom*

The Wills group at Warwick University have developed a number of Ru(II)-based enantiomerically pure catalysts for use in the asymmetric transfer and pressure hydrogenation of ketones and imines.

The latest developments in our programme of development of catalysts for asymmetric reduction will be described in this presentation including;

i) The application of Ru(II)/arene/TsDPEN complexes containing a 'tethering group' for the catalysis of asymmetric hydrogenation of ketones and aldehydes, i.e. using hydrogen gas as the reducing agent in place of transfer hydrogenation conditions.

ii) A new process for the efficient synthesis of a series of 'tethered' Ru(II) catalysts for use in asymmetric transfer and pressure hydrogenation of ketones, and the synthesis of a number of new examples of catalysts. The application of these new catalysts to asymmetric reduction of ketones and imines will be described.

iii) A new class of tridentate ligands for use in Ru-catalysed asymmetric ketone hydrogenation; synthesis, characterisation and applications to asymmetric transformation. The proposed mechanism of action of these new catalysts will be described.

iv) the expansion of our Ru-based catalysts to a range of target substrates, including hindered ketone substrates, C=N bond-containing substrates and aldehydes, unsaturated substrates and substrates containing a substantial level of functionality, including heterocyclic groups.

This will detail the latest developments from our group's research and proposed future research work in this rapidly-developing and challenging research area.

Keywords: *Hydrogenation; Asymmetric catalysis; Reduction; Alcohols; Ruthenium;*

Organometallic Chemistry, catalysis, new frontiers – III

O-081

DESIGN, SYNTHESES AND APPLICATIONS OF TADDOL-DERIVED ASYMMETRIC PHASE-TRANSFER CATALYSTS

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Tartaric acid, TADDOLs and analogous compounds are easily obtained and extraordinary versatile chiral auxiliaries, which have found numerous and widespread applications as chiral ligands in asymmetric metal catalyzed transformations.[1] Surprisingly, their use as chiral organocatalysts has so far been limited to a few applications only.[2]

Thus we started a project aiming at the development of TADDOL derived asymmetric organocatalysts with a special focus on asymmetric phase transfer catalysis (PTC).[3] We recently developed a route to access novel TADDOL-derived N-spiro quaternary ammonium salts which were found to be useful catalysts for the asymmetric a-alkylation of glycine Schiff bases. Further structural modifications of these catalysts are currently underway and applications of these PTCs in other reactions are investigated.

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Keywords: *organocatalysis; Phase-Transfer catalysis; asymmetric catalysis;*

Organometallic Chemistry, catalysis, new frontiers – III

O-082

CATALYTIC MOLECULAR REARRANGEMENTS AS TOOLS FOR C-C BOND FORMATION

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The advent of the 21st century brought about a pressing need for new, efficient and clean strategies for rapid elaboration of molecular complexity. Our group has studied the use of atom-economical transformations, domino pericyclic reactions and redox-neutral rearrangement sequences as particularly appealing means towards achieving those ambitious goals.

In this presentation, we will cover in detail some of our research in these areas. We have been recently interested in the development of an original and concise synthesis of functionalised cyclobutenes,[1,2] exploiting palladium catalysis to manipulate a bicyclic lactone photoproduct. This work has unearthed intriguing aspects of diastereo- and enantioselectivity which are unprecedented in asymmetric allylic alkylation chemistry.[3]

An additional, recent research focus in our team has been the controlled manipulation of sp^3 C-H bonds. The strategy we chose to employ (Scheme 2) takes advantage of the internal redox-reaction of specifically designed tethered amines, which effectively achieves oxidation of the relevant C-H linkage at the expense of a sacrificial, removable oxidant. Applications of this approach to the streamlined total synthesis of relevant natural products will be presented and discussed.[4]

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Keywords: *asymmetric catalysis; deracemisation; total synthesis; alkaloids; C-H activation;*

Organometallic Chemistry, catalysis, new frontiers – III

O-083

SYNTHESIS OF BIOLOGICALLY ACTIVE COMPOUNDS VIA DIRECT ARENE-ASSEMBLING REACTION

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Direct C–H functionalization has garnered significant attention from the synthetic community as an "ideal" method for carbon–carbon and carbon–heteroatom bond formation. Although the development of new reactions and catalysts continues to evolve at a rapid pace, successful applications of this method to the synthesis of natural products and pharmaceuticals are still rare. Thus, our research program focuses on synthesis-oriented methodology development in catalytic C–H coupling.

We developed the transition metal-catalyzed C–H coupling of heteroarenes such as 1,3-azoles, indoles, pyrroles, azines and thiophenes, and applied it to the synthesis of complex natural products and pharmaceutical candidates.

Keywords: *Cross-coupling; Total synthesis; Transition metals; Synthetic methods; C-H activation;*

Organometallic Chemistry, catalysis, new frontiers – IV

O-209

NEW BONDING AND REACTIVITY IN SYNTHETIC CHEMISTRY

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Unlike N-heterocyclic carbenes (NHCs) that are now ubiquitously employed in metal based chemistry, the nitrogen derived analogue - where a carbon is replaced with the isoelectronic nitrogen cation (a nitrenium ion) - has remained elusive as a ligand for metals. This is especially intriguing since a number of other main group analogues of NHCs, such as silylenes, germilenes, phosphenium and arsenium salts, proved to coordinate to transition-metal complexes. We will demonstrate the first example of nitrenium ions as ligands for transition metal chemistry.[1] Preparation, structures, properties and reactivity of metal complexes based on these novel nitrenium ligands will be discussed.

In the second part of the lecture, new types of well-defined halogen bonds will be presented. These non-covalent assemblies were fully characterized in solution and solid state, and their stereoelectronic parameters were evaluated. Moreover, a concept of halogen bond utilization for an activation of the electrophilic substrates in catalysis will be demonstrated.

Keywords: *carbenes; ligand design; homogeneous catalysis; noncovalent interactions;*

Organometallic Chemistry, catalysis, new frontiers – IV

O-210

THE IRON APP – PRACTICABLE IRON-CATALYZED C-C AND C-H BOND FORMATIONS

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Iron is an essential metal for the life cycle of all living things. Mimicking metabolic oxygenations, many protocols for iron-catalyzed oxidations have been reported in the past. The realization of efficient iron catalysis for reductive transformations has only recently gained momentum. Today, iron-catalyzed cross-coupling reactions have been developed to a multi-faceted class of C-C bond-forming reactions with wide substrate scope and significant functional group tolerance.

We wish to report on our recent results in the application of simple iron catalysts to cross-coupling, dehalogenation, and hydrogenation reactions. The operationally simple protocols utilize cheap pre-catalyst and exhibit high sustainability. The catalysts are reactive toward non-activated substrates such as organic chlorides and simple alkenes.

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3. *Chem. Commun.* **2010**, 6350.

Keywords: *iron; cross-coupling; dehalogenation; catalysis;*

Organometallic Chemistry, catalysis, new frontiers – IV

O-211

IRON-CATALYSED, HYDRIDE-MEDIATED REDUCTIVE CROSS-COUPLING

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Iron catalysis has become an increasingly important and powerful method for carbon-carbon and carbon-heteroatom bond formations due to the inherent cost, environmental and toxicological benefits of iron-based protocols.[1] Although the iron-catalysed reduction of carbonyl functionalities is well established, the reduction of olefins is still a challenge.[2] Our research is focussed on the use of bench-stable iron catalysts for the concurrent reduction and functionalisation of olefins.

An iron-catalysed, hydride-mediated reductive cross-coupling reaction has been developed for the preparation of alkanes. Using a bench-stable iron(II) pre-catalyst, reductive cross-coupling of vinyl iodides, bromides and chlorides with aryl- and alkyl Grignard reagents successfully gave the products of formal sp3–sp3 cross-coupling reactions.[3]

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Keywords: *Catalysis; Iron; Hydrogenation; Cross-coupling; Synthetic methods;*

Organometallic Chemistry, catalysis, new frontiers – IV

O-212

USE OF MAGNETITE NANOPARTICLES AS CATALYST FOR C-C AND C-N COUPLING REACTIONS UNDER MICROWAVE IRRADIATION

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Transition metal catalyzed C-C and C-N coupling reactions are among the most important methodologies used in Organic Synthesis nowadays. Palladium and copper catalysts have been exhaustively studied for these reactions, but the use of iron and iron oxides is growing steadily, due to their low cost and versatility.

In our group we are interested in studying the applications of magnetite (Fe_3O_4) nanoparticles as catalysts for C-C and C-N coupling, analogous to Sonogashira and Buchwald-Hartwig reactions. We performed the reaction between phenylacetylene and halobenzenes using ethylene glycol as solvent, potassium carbonate as base and magnetite (5 mol%) as catalyst and found that only iodobenzene was reactive enough to furnish the desired diphenylacetylene under these reaction conditions. The use of bromopyridine also led to the recovery of the starting products. When the reaction between phenylacetylene and iodobenzene in the same conditions was performed under microwave irratiadion, the major products found were ketals derived from iron-promoted water addition to phenylacetylene, followed by ketalization with ethylene glycol.

We further investigated the effect of magnetite over C-N coupling reaction between halopyridines and piperidine and we found that this iron oxide was not able to enhance the products yields further than those obtained without any catalyst.

In resume, we found that although magnetite can be used for C –C coupling of iodobenzene and phenylacetylene, this catalyst failed in promoting the same reaction under microwave irradiation or promoting C-N coupling reactions. On the other hand, it was efficient in promoting the one-step ketalization of phenylacetylene.

Acknowledgement: *The authors wish to thanks CNPq, CAPES and FAPERJ for the financial grant.*

Keywords: *Nanoparticles; C-C coupling; Amination; Iron;*

Organometallic Chemistry, catalysis, new frontiers – V

O-218

CATALYSIS FOR TOTAL SYNTHESIS

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My lecture intends to provide an up-date on our programs concerning the activation of π-systems, most notably alkynes, with the aid of transition metal catalysts. Specifically, I will cover advances in the area of alkyne metathesis, for which new catalysts with a much improved application profile have recently been introduced. These new catalysts are highly active, remarkably selective, and at the same time easy to handle. On the other hand, alkynes are privileged substrates in gold- and platinum catalysis. Recent mechanistic studies in this field and the development of asymmetric variants pave the way to applications of catalytic alkyne activation chemistry to the total synthesis of bioactive natural products of biological significance.

Organometallic Chemistry, catalysis, new frontiers – V

O-219

A MODULAR APPROACH TO CHIRAL IMIDATES: A NEW CLASS OF NITROGEN-BASED CHIRAL LIGANDS

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K. VANDYCK[1]

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Nitrogen-containing ligands are known as ***cheap, readily accessible and stable*** alternatives for phosphane ligands[1], which are often very sensitive to air and require a multistep synthesis [2]. We wish to present a ***combinatorial approach*** to ***a novel type of nitrogen-based mono- and bidentate ligands***[3, 4]. These ligands are characterized by their ***modular structure***, allowing an ***easy one-step synthesis*** by simply combining two readily variable precursors which are either commercially available, or can be reached in only a few steps: a cyclic imidate and a (chiral) amine, respectively diamine. These ligands show ***promising results*** in e.g. the Cu(I)-catalyzed asymmetric aziridination of methyl cinnamate, in asymmetric diethylzinc additions to benzaldehydes, in the Pd(0)-catalyzed asymmetric allylic alkylation and amination, and in Ir(I)-based asymmetric hydrogenation of alkenes.

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Keywords: *asymmetric catalysis; chiral imidate ligands; transition metal catalysis; asymmetric allylic alkylation; asymmetric hydrogenation;*

Organometallic Chemistry, catalysis, new frontiers – V

O-220

TAMING THE REACTIVITY OF ORGANOMETALLIC REAGENTS IN ASYMMETRIC CATALYSIS: NEW VISTAS IN COPPER(I) CHEMISTRY

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The addition of highly reactive organometallic reagents to functionalized substrates is in principle one of the most straightforward methods to construct asymmetric carbon-carbon bond. Copper(I) based catalysts have been used as the synthetic tool *par excellence* to achieve 1,4-selectivity and SN2'-substitution with reactive organometallic compounds such as organozinc, aluminium and Grignard reagents.

This talk will focus on our current discovery which shows that the longstanding paradigm of copper(I) based catalysts favouring 1,4-selectivity over 1,2-selectivity in the addition of Grignard reagents is not fully justified and that highly valuable chiral tertiary and secondary alcohols can be now accessed via copper(I) chemistry.[2] In this talk it will be shown how, employing chiral copper phosphine complex, catalytic enantioselective synthesis of tertiary alcohols can also be achieved for the first time using Grignard reagents with both enones, enals and alkyl aryl ketones with near perfect stereocontrol. Beneficially, the catalytic system provides already the highest level of enantioselectivity using the chiral ligand with *e.r.* of only 60:40. Mechanistic studies, structure of the active species and scope of the reaction will be discussed.

Keywords: *asymmetric catalysis; tertiary alcohol; copper catalysis; ferrocenyl diphosphine; 1,2-addition;*

General synthetic methods – I

O-213

ASYMMETRIC ORGANOCATALYTIC DOMINO REACTIONS

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The research field of organocatalysis has developed rapidly since about the turn of the millennium and can now be seen as a third pillar of asymmetric catalysis beside metal and biocatalysis. Numerous basic organocatalytic protocols for very efficient and highly stereoselective carbon-carbon and carbon-heteroatom bond formations are now part of the strategic arsenal of synthetic chemistry.

In this short lecture the development of simple, triple and even quadruple organocatalytic domino (cascade) reactions[1] using i.a. diphenyl prolinol-TMS-ether as catalyst will be presented. Some applications of these organocascade reactions in the short and efficient asymmetric synthesis of thiadecalines[2], 3*H*-pyrrolo[1,2-a]indole-2-carbaldehydes[3], novel GABA derivatives[4], polyfunctionalized 3-(cyclohexenyl-methyl)-indoles[5] and tetracyclic indol structures will be reported.

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General synthetic methods – I

O-214

ACETYLENES CARRYIN FLUORINATED CARBORATE ANIONS

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One of the best known and most studied among electrically conducting polymers is polyacetylene, which has a long π-conjugated linear polyene backbone and becomes conducting after doping.[1] We try to synthesize deeply doped polyacetylenes carrying the HCB11F11- anion,[2] whose synthesis by direct fluorination of [CsHCB11H11] with elemental fluorine in HF we have improved. This carborate anion is expected to be resistant to oxidation and electrophilic attack. The nucleophile LiCB11F11- generated from [CsHCB11F11] with BuLi or MeOLi was alkylated with acetylene derivatives TMSC=C-CR2--(CH2)n-X (X=Br, I, MsO). The trimethylsilyl group was then removed with CsF in DMF and the desired acetylenes HC=C--CR2-(CH2)n-CB11F11- (R=Me or H) were obtained. We have attempted to polymerize these acetylenes with several common polymerization catalysts but so far have obtained only oligomers.

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Keywords: *carborate anion; polyacetylene; fluorinated;*

General synthetic methods – I

O-215

REGIO- AND STEREOSELECTIVE RING TRANSFORMATIONS OF SMALL-RING AZAHETEROCYCLES VIA AZIRIDINIUM AND AZETIDINIUM INTERMEDIATES

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Three- and four-membered azaheterocyclic systems have acquired a pivotal position as building blocks in organic chemistry. In particular, aziridines and azetidines have been shown to be eligible synthons for the construction of a broad variety of stereodefined heterocyclic frameworks, often endowed with pronounced bioactivities. In this presentation, the synthetic flexibility of functionalized aziridines and azetidines toward the preparation of different types of aza- and oxaheterocyclic structures will be explained. These transformations proceed through the transient generation of mono- and bicyclic aziridinium or azetidinium intermediates, which are intercepted by various nucleophiles in a regio- and stereoselective manner.

Selected examples in that respect include the use of 2-(4-chloro-2-cyanobutyl)aziridines for a microwave-promoted stereoselective rearrangement into 2-(chloromethyl)piperidin-4--carbonitriles[1] and for a one-step $LiAlH_4$-induced transformation into 2-aminomethyl-1-azabicyclo[2.2.1]heptanes, the deployment of 2-(2-cyanoethyl)aziridines for an enzyme-catalyzed rearrangement into 5-hydroxypiperidin-2-ones and for a ring transformation to 4-(aminomethyl)butyrolactones via intermediate 3-(aziridin-2-yl)propanoates,[2] a solvent-mediated selective transformation of 2-bromomethyl-2-methylaziridines into either functionalized aziridines or azetidines,[3] a stereoselective ring enlargement of chiral 2-(1-chloroalkyl)azetidines into 3-chloropyrrolidines[4] and of 2-(2-mesyloxyethyl)azetidines into 4-substituted piperidines,[5] thermodynamically- or kinetically-controlled ring-opening reactions of aziridinium salts by halides,[6] and a peculiar rearrangement of 1-(2-chloropropyl)aziridines into 2-aminopropanes via elusive *N*-spiro bis-aziridinium intermediates.[7]

In summary, a variety of new ring-rearrangement protocols for the selective transformation of aziridines and azetidines into different heterocyclic systems, mediated by the formation of highly reactive strained intermediates, will be presented.

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Keywords: *Heterocycles; Ring expansion; Synthetic methods; Reactive intermediates;*

General synthetic methods – I

O-216

UMPOLED TANDEM REACTION OF ALPHA-IMINO ESTERS

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Nucleophilic addition to the nitrogen atom of simple imines is, in principal, difficult due to the electron negativity of the imino functionality. Only limited examples have been available for the nucleophilic addition to the nitrogen atom of alpha-imino esters. The reactivity of alpha-imino esters is of interest and several intriguing features have been discovered. *N*-Alkylation of the imines derived from glyoxylate esters was conducted with dialkylaluminum chloride in acetonitrile to give an *N*-monoalkylated intermediate, which in turn underwent a subsequent addition reaction with another imine. When the *N*-monoalkylated intermediate was oxidized with BPO in the presence of allyltributyltin or cyanotrimethylsilane, tandem *N*-alkylation-*C*-allylation or *N*-alkylation-*C*-cyanation products were respectively obtained in good yields. Thus, alpha-imino esters behave as acceptors of two nucleophiles which attack across the C=N double bond.

When an imine had two electron-withdrawing groups, *i. e.*, 2-[*N*-(*p*-methoxyphenyl)imino]malonate, this derivative served as an excellent *N*-alkylation reagent for Grignard reagents. Subsequent oxidative removal of the malonate and *p*-methoxyphenyl moieties offered a new amination methodology for carbanions.

In a similar mannner, the alkoxycarbonyl iminium salt is easily prepared using the oxidation of amino ketene silyl acetal with DDQ, and subsequent nucleophilic addition to this iminium species proceeds efficiently to afford the amino esters in good yields. This methodology provides us with a new and easy entry into reactive iminium salts, which are important synthetic intermediates for many nitrogen-containing bioactive compounds.

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Keywords: *Umpolung; Domino reactions; Amino acids; Regioselectivity; Mannich bases;*

General synthetic methods – I

O-217

DECARBOXYLATIVE ETHERIFICATION OF AROMATIC CARBOXYLIC ACIDS

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The regioselective formation of aryl-oxygen bonds is a synthetic transformation of fundamental importance, as the aryl ether moiety is a common motif in many biologically active molecules and functional materials. Traditional synthesis of aryl ethers *via* sp^2-C–O bond formation, *e.g*. nucleophilic aromatic substitutions of haloarenes or the Ullmann coupling of phenols with aryl halides, proceed under harsh conditions which renders them unsuitable for the late-stage derivatization of functionalized molecules. The current state-of-the-art methods are the Buchwald-Hartwig approach for coupling aryl halides with phenols or alcohols in the presence of a palladium or copper catalyst, and the copper-mediated Chan-Evans-Lam coupling of boronic acids and phenols in the presence of oxygen.

We have developed a decarboxylative variant of the Chan-Evans-Lam-type coupling in which aromatic carboxylic acid salts are regiospecifically coupled with alkoxysilanes to form aryl ethers. The bimetallic catalyst system consists of a silver catalyst which allows for the generation of an aryl nucleophile by decarboxylation of an *ortho*-substituted benzoic acid, and of copper(II) acetate that mediates the C–O coupling with alkoxides in the presence of an oxidant. This protocol allows for a regioselective synthesis of aryl ethers from aromatic carboxylates with various electron-withdrawing and donating groups. Thus, diaryl and linear or branched alkyl aryl ethers containing *i.a.* nitro, methoxy, dimethylamino, sulfonyl, chloro, fluoro, trifluoromethyl or phenyl groups in the *ortho*position could be obtained in good yields.

The key advantage of the decarboxylative etherification reaction as a synthetic entry to aryl ethers is that it is based on widely available carboxylic acids as the starting materials, which often have substitution patterns complimentary to those of aryl halides or boronic acids as they draw on different starting material pool.

The new reaction sets the stage for the development of related decarboxylative C–heteroatom bond forming reactions, *e.g.* decarboxylative aminations.

Keywords: *Carboxylic acids; C-C activation; Homogeneous catalysis; C-O coupling; Arenes;*

General synthetic methods – II

O-357

SYNTHESIS OF COMPLEX MOLECULES. PROBLEMS AND SOLUTIONS

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During the synthesis of complex bioactive compounds, some synthetic steps revealed problematic however, these problems were a good source of inspiration to develop methods.

One major challenge to access complex molecules is the design and execution of concise approaches and strategies that are using reactions that rapidly lead to the skeleton framework of natural and/or biologically active compounds. In the case of bioactive complex oxygenated molecules, the problems encountered during their synthesis, forced us to find a solution and to explore their construction by utilizing new conditions involving organometallics to realize coupling reactions, cyclizations as well as diastereo- and enantioselective condensations.

These methods and their applications to the synthesis of biologically active complex natural and non-natural heterocycles will be presented.

Keywords: *total synthesis; bioactive molecules; coupling reactions; organometallics; Natural products; Synthetic methods; C-C coupling; Heterocycles;*

General synthetic methods – II

O-358

TRIANGULENE-DERIVED PUSH-PULL CHROMOPHORES

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Push-pull chromophores consisting of strong donor and acceptor moieties connected through various π-conjugating linkers have attracted much attention due to their strongly bathochromically shifted UV/vis absorption bands as absorbers in bulk heterojunction organic solar cells or as functional dyes for nonlinear optics.[1]

Bridged triphenylamine derivatives, so-called triangulenes, have been realized by *Hellwinkel* and co-workers about 40 years ago.[2] However, the potential of these scaffolds for the construction of π-systems with interesting optoelectronic properties have by far not been exhausted to date. Here, we present the synthesis and optoelectronic properties of a series of novel triangulene chromophores featuring intramolecular charge-transfer interactions.

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Keywords: *Conjugation; Heterocycles; Charge transfer; Chromophores; Fused-ring systems;*

General synthetic methods – II

O-359

HYDROGENATION OF HETEROCYCLIC CALIXARENES

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The simple and efficient synthesis of calix[4]furan and calix[4]pyrrole has been known for more than 125 years. The connectivity of the heterocyclic calix[4]arenes is identical with the skeleton of the «pigments of life». The chemical properties, especially the ability to form complexes with transition metals, are totally different when comparing the artificial systems with the natural products. A direct way to confer metal binding capabilities to compounds derived from heterocyclic calix[4]arenes is hydrogenation. We present our systematic studies of the hydrogenation reactions of calix[4]furan and calix[4]pyrrole. The hydrogenation of the calix[4]pyrrole proved to be challenging. The major products obtained first were the half reduced macrocycles of the type calix[2]pyrrole[2]pyrrolidine. The totally reduced macrocycle was isolated only in small amounts. To understand the sequence of this heterogenous catalytic hydrogenation the synthesis of mixed calix[n]furan[4-n]pyrrole was undertaken. These mixed macrocycles were good model compounds for studying the sequence of the reduction process. The macrocycles were preferentially hydrogenated on the furan rings, whereas the hydrogenation of the pyrrole rings consistently needed much harsher conditions. Exploiting this difference in reactivity we were able to determine the sequence of the hydrogenation reaction. Based on these mechanistic data an improved synthetic procedure has been developed for the hydrogenation process, which allowed us to obtain the totally reduced macrocycle calix[4]pyrrolidines in quantitative yield. The calix[2]pyrrole[2]pyrrolidine showed a very strong intramolecular hydrogen bond network. This network determines the structure, the conformational behavior and the chemical reactivity of this novel macrocycle. The metal binding of the totally reduced calix[4]pyrrolidines will be presented. The new calix[4]pyrrolidines can be classified as new stiffened macrocyclic crown ethers or as saturated analogues of the porphyrin derived «pigments of life».

Keywords: *Heterogenous catalysis; Calixarenes; Hydrogenation; Hydrogen bonds; Heterocycles;*

General synthetic methods – II

O-360

ONE-POT NUCLEOPHILIC RADICAL ADDITION TO KETIMINES GENERATED IN SITU

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In the last years we reported that the Ti(III)/hydroperoxide (H_2O_2, t-BuOOH) system was able to promote both radical Mannich-type reactions and a radical version of the Strecker synthesis, starting from an aldehyde and an amine in ether, alcohol or formamide co-solvent, respectively.[1] The optimization of the previously reported protocol allowed us to develop the nucleophilic free radical addition of formamide to ketimines generated in situ by replacing the aqueous solution of $TiCl_3$ with the more convenient and efficient Ti(IV)-Zn system, providing instant access to quaternary α-aminonacid precursors.[2, 3] The new catalytic system was successfully applied for the nucleophilic radical hydroxymethylation of ketimines, leading to the synthesis of β-amino alcohols[4] and the selective radical aminoalkylation of ethers.[5]

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Keywords: *Radical reactions; Titanium; Multicomponent reactions; Nucleophilic addition; Amino alcohols;*

General synthetic methods – III

O-361

RECENT DEVELOPMENTS OF NEW STEREOSELECTIVE MULTIPLE BOND-FORMING TRANSFORMATIONS

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The presentation will be devoted to some of our recent contributions on the utilization of activated carbonyls towards the development of new MBFTs involving organocatalyzed asymmetric Michael addition, selective intramolecular trapping of iminiums and microwave-promoted both olefin metathesis and acyl-Wolff rearrangement allowing the facile preparation of polyheterocyclic systems with a high level of complexity and diversity.

Keywords: *Michael addition; Multicomponent Reactions; Carbanions; Molecular diversity; Synthetic Methods;*

General synthetic methods – III

O-362

PREPARATIONS OF REGIOSELECTIVELY MONOSUBSTITUTED ALPHA-, BETA- AND GAMMA-CYCLODEXTRIN DERIVATIVES – PRECURSORS FOR FURTHER SYNTHESIS.

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Alkylation of α-, β- or γ-cyclodextrin with allyl, cinnamyl or propargyl bromide followed by peracetylation of remaining hydroxyl groups and separation of isomers resulted in the sets of peracetylated 2^I-O-, 3^I-O- and 6^I-O-alkylated cyclodextrins. Ozonolyzis or oxidative cleaveage of peracetylated allyl or cinnamyl derivatives resulted in complete sets of peracetylated 2^I-O-, 3^I-O- and 6^I-O- formylmethyl or carboxymethyl derivatives which are, as well as the propargyl derivatives, useful precursors for preparation of regioselectively monosubstituted derivatives of cyclodextrins. All compounds were characterized by 2D-NMR techniques. The carboxymethyl derivatives were used as chiral selectors in capillary electrophoresis. Substantial differences in separation abilities among the regioisomers were observed. Thus, the importance of performing supramolecular interaction experiments with pure regiosomers of cyclodextrin derivatives was confirmed.

Keywords: *cyclodextrins; synthetic methods; electrophoresis; NMR spectroscopy; supramolecular chemistry;*

General synthetic methods – III

O-363

CONVENIENT SILYLATION OF PHENOLS BY USING CHLOROSILANES IN BR/MG-EXCHANGE REACTION

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Preparation of aryl Grignards bearing unprotected OH group in halogen-magnesium exchange reaction represent a synthetic chalenge.[1, 2] Some literature data for preparation of trialkylsilyl-substituted phenols by other synthetic methods are available, however, there is no reports on direct preparation of silyl-substituted phenols bearing one or two hydrogen atoms on silicon atom. Namely, such compounds are usually unstable under reaction conditions and readily lose silyl functional group by forming phenols.

Herein, we wish to report efficient direct silylation of bromo-substituted phenols in a Br/Mg-exchange reaction by using various disubstituted chlorosilanes in presence of catalytic amounts of LiCl.[2] Chlorosilane act at the same time as Lewis acid activating magnesium for bromine exchange to *in situ* generate Grignard reagent, and as an electrophilic reagent. By applying this method we successfully isolated various substituted alkylsilyl-, dialkylsilyl-, alkylphenylsilyl- and diphenylsilylphenols in satisfactory to good yields. This approach can be also extended to various heterocyclic compounds bearing a hydroxy group like pyridines and quinolines.

Recently we have found an efficient direct catalytic transformation of some silyl hydrotrioxides (ROOOH).[3] To prepare some polymer-bound silylated substrates we were challenged with the preparation silyl-substituted phenols. In this contribution attempts to prepare polymer-bound substrates via silyl-substituted phenols will also be discussed.

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Keywords: *Grignard reaction; Silanes; Electrophilic substitution; Synthesis design; Polymers;*

General synthetic methods – IV

O-364

C-H ACTIVATION REACTIONS AT SP²- AND SP³-CARBON CENTERS

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C-H activation reactions at sp^2-carbon centers allow for the direct, regioselective introduction of substituents into arenes and hetarenes. Particular focus of our work in this area is the installation of alkyl groups into biologically relevant heterocycles.[1] In the area of C-H activation at sp^3-carbon centers we have studied the diastereoselective amination reaction in the benzylic position of chiral substrates.[32] One of the ultimate goals in C-H activation chemistry is the regio- and enantioselective activation of aliphatic C-H bonds. Towards this goal, we have developed transition metal catalysts, to which a ligand with a hydrogen bonding site is attached.[3] Hydrogen bonding allows to perfectly position the substrate in an enzyme-like approach. Most recent results will be discussed.

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Keywords: *amination; C-H activation; enantioselectivity; homogenous catalysis; hydrogen bonds;*

General synthetic methods – IV

O-365

THE SYNTHESIS OF GIANT CALIXARENES

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Calixarenes are a versatile class of cyclic oligomers successfully applied to ions recognition, for example, thanks to their tunable cavity and their ability to be readily functionalized. Their synthesis involves a reaction between formaldehyde and positions *ortho* to the hydroxyl group of phenol derivatives under basic or acidic catalysis. The ring shape of calixarenes is induced by intramolecular H-bonding as oligomers grow. Among calixarenes family, the most studied are those including 4 to 8 monomer units since they are easily accessible from standard synthesis methods. Very few examples of larger calixarenes are available in the literature and the larger one, synthesized in very small amount, doesn't exceed 20 units. We propose here the synthesis of "giant calixarenes" with a size well above the current state of art. These macrocycles are obtained easily in one step and can be purified by simple selective precipitation processes. We found that, depending mainly on the choice of *para* group and catalyst, and on reaction time, calixarenes are able to reach unsuspected size. In contrast with the classic synthesis of macrocyclic polymers, needing a high dilution to prevent an intermolecular linkage, the giant calixarenes are obtained using a high concentration and produced in very large scale (above 50 g in a 1L-flask). Furthermore, taking advantage of the chemical versatility of calixarenes, we successfully performed the functionalization of giant calixarenes lower rims with different reactants. These new compounds represent a very promising platform for the design and the production of functional macrocyclic polymers, and will probably open new perspectives in material science.

Keywords: *Calixarenes; polymers; macrocycles;*

General synthetic methods – IV

O-366

FROM IMIDAZOQUINOLINES TO IMIDAZOQUINOLINES THROUGH TRICYCLIC QUINOLINES

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2-Aminoimidazoquinoline, compounds with interesting biological properties, was found, like similar pyrazinoquinolines, in thermally treated meats (HCA, heterocyclic amines).[1, 2] The synthetic strategy leading to them is based on closing the quinoline or the azole/pyrazine ring.

Aminobenzimidazoles/triazoles/selenadiazoles/ /quinoxalines we prepared mainly from the corresponding nitroderivatives. After reduction to corresponding amine and applying the Gould-Jacobs protocol with activated enolethers under S_NV conditions we obtained aminoethylene derivatives – precursors of target compounds. Thermal cyclization of the aminoethylenes gave exclusively the angularly annelated azolo/pyrazinoquinolines, which could be converted to parent, non-substituted heterocycles by following reactions: hydrolysis, decarboxylation, chlorination/aromatization and dechlorination.

During reductive dechlorination of the 7-chloropyrido[2,3--*f*]quinoxaline we found that an unknown coupled ring contraction of the fused pyrazine ring into a condensed imidazole ring takes place. The ring transformation of condensed selenadiazole ring gave us a tool to prepare various selectively alkylated tricyclic heterocycles. Another approach afforded food borne carcinogen, 2-amino-3-methylimidazo[4,5-*f*]quinoline (IQ) obtained in total 20% yield using unique strategy.

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Keywords: *imidazoquinoline; selediazoloquinoline; pyrazinoquinoline; nucleophilic vinylic substitution; Gould-Jacobs reaction;*

General synthetic methods – IV

O-367

WATER MEDIATED PROTON-COUPLED ELECTRON TRANSFER IN ENZYMES AND IN FREE-RADICAL CHEMISTRY BY COORDINATION TO METAL COMPLEXES

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Efficient proton and electron transfer lies at the heart of the remarkable success of energy conversions in photosynthesis and respiration. In many biological systems proton transfer (PT) is coupled to electron transfer (ET) allowing the assembly of thermodynamically favored reaction pathways, and avoiding high-energy intermediates.

Here we show theoretical evidences of an unprecedented water mediated long-range PCET process between metal complexes.[1] Water mediates the long-range proton-coupled electron transfer between two Cu complexes separated by 11 ? in the peptidylglycine α-hydroxylating monooxygenase (PHM) cofactor. The proposed mechanism, which involves three H-atom exchanges, accounts for long-range electron transfer in metalloenzymes, and may be ubiquitous in nature.

Taking into account that aquo or hydroxo complexes of other transition metals are generally present in vital processes in nature, those complexes could also play an essential role in many organic synthetic reactions. In this sense, water would be an extraordinary safe and cheap hydrogen atom transfer (HAT) reagent in the reduction of carbon-based radicals. Therefore in recent years solid evidence of HAT reductions involving water as hydrogen atom source have been presented.

Water becomes an excellent hydrogen atom donor in the presence of bis(cyclopentadienyl)titanium(III) chloride (Cp_2TiCl) towards carbon radicals. In this work we also show that the efficiency of Ti(III) aqua complexes as an unique class of HAT reagents is based on two key features: (**a**) excellent binding capabilities of water towards titanocene(III) complexes and (**b**) a low activation energy for the HAT step.[2]

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Keywords: *Density functional calculations; Hydrogen transfer; Metalloenzymes; Radical reactions; Water chemistry;*

General synthetic methods – IV

O-368

CASCADE REARRANGEMENT OF ENEDIYNES WITH MEMORY OF CHIRALITY

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During the past decade, Memory of Chirality (MOC) has emerged as a powerful tool in organic synthetic.[1] This strategy allows the enantioselective construction of a chiral tetrasubstituted stereocenter. We have recently developed a polar/radical crossover cascade rearrangement of enediynes bearing a sulfone moiety as a precursor of an intermediate enyne-allene.[2-3] The reaction proceeded with retention of the configuration of the starting material to afford tetracyclic heterocycle with high memory effect. Deuterium labelling and theoretical calculations were used to demonstrate that an 1,5-hydrogen atom transfer was exclusively involved in this cascade.[4]

Heterocyclic analogues of aspartic esters bearing two contiguous quaternary stereogenic centers were also reached through copper catalyzed five-step cascade rearrangement of terminal enediynes with diazoesters.[5] The copper carbenoid acts as a reactant and catalyst to promote carbene insertion and one-pot allene formation.

In order to overcome the lack of diastereoselectivity which is the main drawback of this process, we devised a tandem Crabbe homologation-radical rearrangement of terminal enediynes leading the synthesis of six- and seven-membered ring α-aminoesters.[6]

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Keywords: *Memory of chirality; Enediynes; Myers-Saito cyclization; Radical cascades; Tetrasubstituted stereocenters;*

General synthetic methods – V

O-369

NUCLEOPHILE SELECTIVE CROSS-COUPLING REACTIONS

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In cross-coupling reactions, the reactivity of the electrophilic functional group typically decreases in the order I > OTf > Br > Cl. This enables reactions to be performed with a very high degree of chemo selectivity.

In contrast, nucleophile selective cross-coupling reactions, where there is a differentiation between different nucleophilic groups, have received little attention to date.

We wish to report a systematic investigation into a cross-coupling procedure with complete differentiation between two nucleophilic sites, a boronic ester and a stannyl group.[1] We will discuss the synthesis of the starting materials and potential applications in materials science.

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Keywords: *cross-coupling; heterocycles;*

General synthetic methods – V

O-370

SOLID-PHASE SYNTHESIS OF DIVERSELY CONSTRAINED PEPTIDOMIMETICS

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Methodology providing access to an array of diverse secondary structure peptidomimetics, with complete control of their stereochemistry, is an indispensable tool for investigation complex structure-function relationships of biologically significant peptides and proteins, and also to obtain highly active and selective compounds with enhanced proteolytic stability.[1] In particular, tandem *N*-acyliminium ion cyclization – nucleophilic addition, which represents a powerful strategy to generate fused-ring systems, has been useful to synthesize constrained peptidomimetics.[2] The concept of these tandem cyclizations inherently enables sequential and independent synthesis of the lineal precursors for cyclic iminiums followed by incorporation of precursors for the nucleophilic addition, allowing the combination of the precursors of both rings to produce combinatorial libraries. The aim of this work has been to develop a general methodology for efficient and expeditious solid-phase synthesis of diversely constrained peptidomimetics, in which the constraints would be assembled from simple building blocks using the *N*-iminium chemistry during solid-phase synthesis, rather than typical incorporation of pre-formed scaffolds. Thus a library of varied heterocycles with functional as well as skeletal diversity was efficiently synthesized with full stereocontrol, achieving several ring sizes and including different internal nucleophiles (N, O, S, C). The analysis of these experiments allowed to recognize the internal nucleophile's requirements to promote the second cyclization, concluding in the case of *N* nucleophiles that sulfonamides achieved the best results. In addition a strong influence of the different tested aminoacids in products' stereochemistry was observed, mainly of those aminoacids present in the first ring. All the fused-rings generated are available to be introduced in a larger peptide, but are also interesting *per se*, being their biological activity measurement in process.

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Keywords: *Fused-ring systems; Heterocycles; Solid-phase synthesis; Peptidomimetics;*

General synthetic methods – V

O-371

TRIPHENYLAMINE BASED D-A OR D-A-D P CONJUGATED SYSTEMS AS MOLECULAR DONORS FOR ORGANIC SOLAR CELLS

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The development of organic solar cells (OSCs) is currently the subject of considerable interest. OSCs based on bulk heterojunctions between conjugated polymers (electron donor material) and fullerene derivatives (electron acceptor material) have led to significant improvements over the last decade. On the other hand, small conjugated molecules represent attractive donor materials since their synthesis is more reproducible, their purification easier and they offer the advantage of being used for both the preparation of bilayer-type OSCs by vacuum deposition and the elaboration of bulk heterojunction OSCs by spin casting.[1] An interesting approach to synthesize efficient donor molecules relies on the introduction of an electron acceptor group A in the structure of the conjugated system to create an intramolecular charge transfer between an electron-donor group D and the acceptor A.[2] Thus D-π-A and D-π-A-π-D systems generally display a broad absorption in the visible spectrum and they have recently shown interesting performances in both bilayer and bulk heterojunction OSCs. In this context, we present here the synthesis and characterization of new symmetrical and unsymmetrical D-π-A-π-D molecules based on tetracyanobutadiene as central acceptor (A) and oligothienyl-TPA chains as donors (D),3 as well as new D-π-A systems of minimized length based on a bridged indenothiophenone derivative as acceptor. OSCs of simple bilayer architecture made with these new compounds show photovoltaic conversion efficiencies ranging from 1 to 3% which represent very promising results.[3, 4]

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Keywords: *organic electronics; thiophene; organic solar cells; sulfur heterocycles;*

General synthetic methods – V

O-372

JANUS-HEAD TYPE DIPHOSPHORUS TRICATION $[PYR_3P_2]^{3+}$ (PYR = 3,5-DIMETHYLPYRAZOLE) AS REAGENT FOR THE FUNCTIONALISATION OF ORGANIC MOLECULES

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Main group element-centered cations possess unusual reactivities.[1] Especially, multiply charged phosphorus-centered cations are comparable rare[2] and we have found that certain types of these cations can be used for unusual bond formation reactions. Recently, we reported on a Janus-head type diphosphorus trication $[pyr_3P_2]^{3+}$ (1) as triflate salt ($1[OTf]_3$).[3] Due to the high Lewis-acidity and the presence of the labile pyrazolyl moieties in this compound, we found that this highly-charged, very oxophilic cation 1^{3+} allows unusual phosphorus-oxygen bond formation reactions.[3, 4] In this context we became interested in using compound $1[OTf]_3$ as deoxygenation and pyrazole transfer as well as dehydration reagent in organic synthesis. Hence $1[OTf]_3$ enables us to functionalise organic compounds such as pyridones, urea-compounds or amides in a one-pot syntheses. We will present our recent results and discuss possible applications of our approach.

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Keywords: *Phosphorus; Sustainable Chemistry; Green Chemistry; Functionalisation; Amides;*

General synthetic methods – V

O-373

CU CATALYZED SELECTIVE MONO-N-PYRIDYLIZATION: 2-AMINODMAP/SULFONAMIDES AS BIFUNCTIONAL ORGANOCATALYSTS

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Chiral DMAP analogues offer unique reactivity and versatility as Lewis base catalysts in a wide array of reactions.[1] There is a significant demand to evolve novel practical methodologies targeting direct mono-*N*-functionalization of C_2-symmetrical diamines.Herein, we have anticipated that the chiral 2-aminoDMAP derived from *trans*-cyclohexane-1,2-diamine could serve as a versatile Lewis basic catalaphore and introduction of various H-bond donor entities *via* modification of remaining primary amine might led to discovery of new reactivities in context of bifunctional acid/base catalyst development. For this purpose, we have explored the possibility of Pd-catalyzed Buchwald-Hartwig *N*-arylation[2] of the (1*R*,2*R*)-cyclohexane-1,2-diamine with 2-haloDMAPs. However no trace of target compound was observed. Realizing unsatisfactory results with palladium chemistry, we have turned our attention to copper-catalyzed modified Ullmann coupling reaction. Successful synthesis of 2-aminoDMAP readily in only one step encouraged us to investigate the catalytic potential of this basic catalaphore unit in pursuit of efficient bifunctional acid/base organocatalysts.[3] Sulfonamides were chosen to chaperon 2-aminoDMAP base as the H-bond donor counterpart. Developed catalysts were screened in conjugate addition of acetylacetone to *trans*-(β)-nitrostyrene, serving testing ground for bifunctional organocatalysis. We presented 10 examples of bifunctional acid/base organocatalysts incorporating 2-aminoDMAP and systematically varied sulfonamide moieties. The catalyst given above was shown to promote the conjugate addition reaction of acetylacetone and *trans*-(β)-nitrostyrene effectively with enantioselectivites up to 93%.

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Keywords: *copper; organocatalysis; asymmetric synthesis;*

General synthetic methods – V

O-374

MULTIPLE ARENE FUNCTIONALIZATION USING TRANSIENT DIAZONIUM SALTS

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Arene diazonium salts have emerged as versatile coupling reagents in numerous Pd-catalyzed reactions.[1] A particular benefit of these reagents is the very high reactivity, the opportunity to suppress undesired double bond migration following Heck reactions,[2] and their convenient and economically advantageous synthesis from anilines. However, there are also a few disadvantages that often deter chemists from using these reagents: quite often the anilines are remarkably sensitive towards oxidation, and handling isolated diazonium salts is often considered as potentially hazardous.

Over the past few years we have embarked on a project directed at using anilides rather than anilines as precursors for arene diazonium salts. This approach involves the in situ deacetylation, diazotation and precipitation as stable isolable tetrafluoroborates.[3] In this contribution we report about the extension of this sequence by Pd-catalyzed steps, leading to the establishment of anilides as electrophile precursors for Heck- and cross coupling reactions. We will further report how this methodology can be used for the synthesis of phenolic natural products with minimization of protecting group steps (using phenol diazonium salts as arylating agents)[4, 5] and for the synthesis of polyfunctionalized naphthalines. Finally, our first results on the efficient double exploitation of acetanilides as directing groups in dehydrogenative Heck reactions and as leaving group precursors in conventional Heck reactions will be presented.[6]

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Keywords: *Arenes; C-C coupling; Diazo compounds; Palladium; Synthetic methods;*

Natural products, Drugs – I

O-479

SYNTHETIC ANTITUMOR VACCINES BASED ON MUCIN GLYCOPEPTIDE ANTIGENS

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Membrane glycoproteins of epithelial tumor cells show glycosylation patterns which are quite different from those of normal cells. Among those, tumor-associated mucin MUC1 is highly over-expressed on tumor cells and characterized by short, prematurely sialylated saccharide antigens. Glycopeptides of the extracellular tandem repeat region of MUC1 carrying the Tn- T-, Sialyl-Tn-, and Sialyl-T-antigen saccharides are considered promising target structures for a selective immunological attack on epithelial tumor cells.

In order to construct synthetic vaccines, Fmoc-protected O-glycosyl threonine and serine building blocks containing these tumor-associated saccharide antigens were synthesized and applied to solid-phase syntheses of tumor-associated MUC1 glycopeptides. These glycopeptides were coupled to T cell epitope peptides from ovalbumin[1] to furnish fully synthetic vaccines **A**. Antibodies induced by these vaccines **A** in transgenic mice showed a high selectivity in binding to MUC1 glycopeptide antigens.

In addition, the tumor-associated MUC1 glycopeptide antigens were conjugated to Tetanus Toxoid to give highly immunogenic vaccines.[2, 3] Immunization with these vaccines elicited antibodies which strongly bound to tumor cells in culture and in tissues.

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Keywords: *Synthetic vaccines; Glycopeptides; Solid-phase synthesis; Mucin MUC1;*

Natural products, Drugs – I

O-480

SYNTHESIS OF BIOLOGICALLY IMPORTANT OLIGOSACCHARIDES CONTAINING ALPHA(2,8)OLIGOSIALIC ACIDS

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α(2,8) Oligosialic acids are frequently located at the non-reducing end of biologically active glycoconjugates such as glycoproteins and glycolipids. Ganglio-series gangliosides are a family of glycolipids involving a tetrasaccharide (Galβ(1,3)GalNAcβ(1,4)Galβ(1,4)Glc) bearing α(2,8) di/oligosialic acids at the 3-position of the both galactose moieties. They further are classified by the presence of the sialic acid residues linked to the inner galactose moiety; one (a-series), two (b-series), and three (c-series). GP1c glycolipid is one of the most complex c-series gangliosides involving α(2,8) tri- and di-sialic acid units.

Chemical synthesis of these di-/oligo-sialo-containing glycolipids and their derivatives would facilitate identification of their biological roles. However, synthesis of both the α(2,8) oligosialic acid unit and the compact and rigid 3,4 dibranched galactoside unit is challenging. We recently reported on a new and effective method for α-sialylation using the 5,4-*N*,*O*-carbonyl protected sialyl donor, which enabled preparation of α(2,8) and α(2,9) tetrasialic acid in stereoselective manner. The 5,4-*N*,*O*-carbonyl protection permitted a-sialylation without use of nitrile solvents. Herein, we report the synthesis of a set of the ganglio-series of ganglioside epitopes varying the number of sialic acid residues.

Keywords: *ganglioside; sialic acids; glycosylation; library;*

Natural products, Drugs – II

O-481

BIOINSPIRED CHEMISTRY WITH PEPTIDES

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In nature, proteins fulfill manifold different functions and are crucial as, for example, enzymes or templates for the controlled formation of structural components such as bones or seashells. My research group is intrigued by the question whether also peptides with significantly lower molecular weights compared to proteins, can fulfill functions for which nature evolved large macromolecules. For example, we are engaged in the development of peptides as asymmetric catalysts and templates for the controlled formation of inorganic nanoparticles.

1. Tripeptides of the general type H-Pro-Pro-Xaa (Xaa = amino acid with a carboxylic acid) are effective catalysts for aldol reactions[1, 2] and conjugate addition reactions between aldehydes and nitroolefins.[3, 4] The peptides allow for enamine catalysis with catalyst loadings of as little as 0.1-1 mol % and provide the synthetically versatile products in high to excellent stereoselectivities. The scope of these peptide catalyzed reactions will be presented.

2. The development of peptides as templates for the controlled formation of silver nanoparticles (AgNPs) in defined sizes will be presented. Utilizing combinatorial chemistry different tripeptides were identified that allow for the formation of AgNPs in significantly different sizes.[5] More recently, a correlation between the length of oligoproline-based templates and the size of the resulting AgNPs was observed.[6]

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Keywords: *Peptide; Nanoparticles;*

Natural products, Drugs – II

O-482

PEPTIDO SULFONYL FLUORIDES AS NEW PROTEASE INHIBITORS

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We have employed the sulfonamide moiety as a transition-state isostere of the hydrolysis of the amide bond. Incorporation of the sulfonamide moiety led to peptidosulfonamide-peptide hybrids capable of protease inhibition or resistant to proteolytic degradation. The versatile preparation of b-peptidosulfonamides, in which all peptide-amide bonds have been replaced by sulfonamide moieties, enticed investigation of the foldamer properties of this class of peptidomimetics.

We have found that the required amino acid derived sulfinyl chlorides or amino acid derived sulfonyl chlorides intermediates can also be employed for the preparation of new "electrophilic traps" useful for the synthesis of protease inhibitors. Thus, amino acid based sulfinyl chlorides were converted into the corresponding a-chloromethylsulfoxides capable of inhibition of for example papain. Moreover, amino acid derived sulfonyl chlorides could be converted into the corresponding sulfonyl fluorides, which are crucial building blocks in the preparation of peptido sulfonyl fluorides comprising a new class of protease inhibitors. Apart from inhibition of chymotrypsin, protease activity of the proteasome can be efficiently inhibited. This offers opportunities for using peptido sulfonyl fluorides as powerful selective protease inhibitors in cancer treatment but also as potential anti-malaria compounds. Both the presence of a peptide fragment and the amino acid derived sulfonyl fluoride offer great possibilities for profiling but also for tuning the reactivity and specificity of the protease of interest.

Natural products, Drugs – III

O-483

PHYTOHORMONES AS LEADS FOR ANTICANCER DRUG DEVELOPMENT

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Throughout history, natural products have afforded a rich source of compounds that have found many applications in the fields of medicine, pharmacy and biology. Our research focused on cell division cycle showed that natural phytohormones cytokinins are also rather non-specific inhibitors of various protein kinases. Surprisingly, among aromatic cytokinin derivatives, 2-(2-hydroxyethylamino)-6-benzylamino-9-methylpurine, named olomoucine (OC), which specifically inhibits some CDKs at micromolar concentration was discovered. The total lack of the inhibitory effect of olomoucine on major kinases, such as cAMP- and cGMP-dependent kinases, protein kinase C, and others, suggests that OC might be a useful tool for cell cycle regulation studies. The design and inhibitory activity of OC was further improved by modifications at positions 2, 6, and 9, i.e., the positions that control binding to CDK1. This led to discovery of novel specific CDK inhibitors named roscovitine, olomoucine II, purvalanol A, and LGR1406, which display an enhanced inhibitory activity toward CDK1, a higher selectivity toward some CDKs, an increased antimitotic activity at the G1/S and G2/M points of the cell cycle, and stronger and more selective antitumour effects. The compounds are also effective *in vivo* and one of them is already in clinical trials in USA and Europe (roscovitine ? Seliciclib, Cyclacel Pharmaceuticals Ltd, U.K.). Seliciclib is currently in Phase IIb clinical trials as a single therapy in multiple myeloma as well as two other B-cell hematological malignancies: B-cell Chronic Lymphocytic Leukemia and Mantle Cell Lymphoma. An additional Phase IIb clinical trial is in progress investigating the effects of Seliciclib in patients with Non-Small Cell Lung Cancer in combination with gemcitabine and cisplatin. Recently, we have developed also first CDK9 inhibitors and discovered whole range of new structural motifs for development of CDK inhibitors which are derived from anticytokinin structures.

Natural products, Drugs – III

O-484

CHEMICAL AND BIOLOGICAL POTENTIAL OF NEW AZETIDINONE DERIVATIVES

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Beta-lactam compounds are really "evergreen" molecules. Beside bicyclic b-lactam substrates such as penicillins, cephalosporins, and carbapenems, monocyclic compounds, azetidinones, emerged for their interesting and variegated biological activities.[1] We developed the synthesis of a new class of monocyclic b-lactam derivatives, 4-alkyliden-azetidinones, characterized by a C=C bond on the C-4 position of the ring.[2] 4-Alkyliden-azetidinones proved to be interesting scaffold for antibiotics against resistant bacteria[3] and effective enzymatic inhibitors against Human Leukocyte Elastase (HLE) and matrix metallo-proteases (MMPs), and as antiaggregating agents.[4] In exploring their use as synthons we observed that the C=C double bond in 4-alkyliden-azetidinones revealed an unexpected characteristic of low reactivity towards addition reactions of electrophiles or nucleophiles, whereas we succeeded in an unexpected oxidative substitution of vinylic hydrogen or halodecarboxylation reaction which led to the synthesis of mono and di-vinylhalides of 4-alkylidene-azetidinones.[5]

Our interest in the design of new beta lactam compounds with specific biological activities recently allowed us to extend our strategies to the synthesis of new monocyclic derivatives with specific inhibitory potency against integrins and histone deacetylase enzymes (HDAC).[6]

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Keywords: *Lactams; Inhibitors; Synthesis Design; Small ring systems; Heterocycles;*

Natural products, Drugs – III

O-485

NOVEL ANIONIC STEROID INHIBITORS OF PHASICALLY AND TONICALLY ACTIVATED NMDA RECEPTORS

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N-methyl-D-aspartate receptors (NMDARs) play important roles in development, synaptic plasticity, learning, and memory, however, abnormal activation of NMDA receptors is thought to mediate neuronal degeneration. NMDA Receptor activity can be influenced by exogenous and endogenous ligands, including neurosteroids - endogenous steroids that are synthesized and act in the central nervous system. 20-Oxo-5β-pregnan-3α-yl sulfate (pregnanolone sulfate; PA-S) is an endogenous neurosteroid that inhibits NMDARs and is neuroprotective. However, the low bioavailability and poor metabolic stability of PA-S limit its *in vivo* application. Therefore, we have prepared a series of new pregnanolone derivatives bearing negatively charged substituents at C-3 connected via linkers of various lengths. As such, pregnanolone 3α-hemiesters of oxalic, malonic, succinic, glutaric, adipic, pimelic, and suberic acids were prepared. Subsequently, the patch-clamp and imagining recordings from HEK293 cells expressing NR1/NR2B receptors and cultured rat hippocampal neurons were used to establish the NMDARs inhibition and IC_{50} values. We conclude that the values of IC_{50} assessed for novel synthetic C-3 analogs of PA are correlated with the length/lipophilicity of the substituents at C-3. Moreover, we have showed that these compounds differ by a rate of inhibition of tonically and phasically activated NMDA receptors. Defining the properties of pharmacophore for pregnanolone inhibitors of NMDA receptors and improving inhibitor pharmacological properties could bring practical results in the treatment of serious neuronal diseases and disorders such as brain injuries, consequences of brain stroke, epilepsy, and in a number of others.

Keywords: *steroids; receptors; lipophilicity; Structure-activity relationships; Drug design;*

Natural products, Drugs – III

O-486

CHEMOENZYMATIC NATURAL PRODUCT SYNTHESIS

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Biocatalytic approaches towards new building blocks for organic synthesis have increa-singly emerged as an important tool in recent years. Nowadays, a number of biotrans-formations are primarily applied in the chemical and pharmaceutical industries delive- ring fine chemicals, e.g. for drugs. The mild reaction conditions - also triggering high stereo-, regio-, and chemoselectivity - and the often elegant short-cuts in synthetic en-deavours lead to economic and ecological advantages of the enzymatic conversions.[1]

The focus of our projects is on natural product syntheses and the development of new synthetic methods (see e.g. ref.[2]). The synthesis of the highly selective antitumor reagent psymberin (Figure 1), isolated from the sponge *Psammocinia spp*.,[3] is one of the more recent target molecules in our group, but also marine oxylipins such as the constanolactones caught our attention. The progress on a chemoenzymatic approach towards key building blocks for organic synthesis will be presented. Enzymes utilized range from hydrolases, aldolases and (ene)reductases to monooxygenases.

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Keywords: *Biocatalysis; Asymmetric catalysis; Natural products; Total synthesis;*

Natural products, Drugs – III

O-487

CASE STUDIES OF ASYMMETRIC HYDROGENATION OF CHALLENGING PHARMACEUTICALLY RELEVANT SUBSTRATES

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Two recent case studies of asymmetric hydrogenation of unusual and challenging pharmaceutically relevant substrates will be presented. Emphasis on challenges of industrially applicable catalytic transformations will be given.

First case study will show efficient asymmetric hydrogenation of (1-chlorovinyl) boronates.[1]

Broad range of substituted (1-chlorovinyl) boronates, with different steric and electronic properties, can be successfully hydrogenated in the presence of P^N-iridium catalysts without significant cleavage of the C-Cl bond.

It will be shown how rational modification of the structural properties of the P^N ligands can result in new N-acyl-imidazoline ferrocenyl-based iridium catalysts with broad substrate acceptance. With these catalysts, excellent conversions, high chemoselectivities (with dechlorinated byproducts in the range of 3–19%), and enantioselectivities of up to 94%ee can be obtained. The utility of the hydrogenation method presented will be demonstrated on preparation of a key precursor for the construction of the anticancer drug bortezomib.

Second case study will deal with development of asymmetric hydrogenation of a pyridyl benzo thiophene alkene.[2] Studied transformation represents a key step in enantioselective synthesis of NBI-75043, a selective and potent H1 antagonist for the treatment of insomnia.

Reduction can be successfully accomplished using [BoPhoz Rh] catalysts. By tailoring the steric properties of the BoPhoz ligand, the ee of the product can be increased from just 12% to 90%. This research further expands the substrate scope of the conventional class of functionalized alkenes amenable to catalytic asymmetric hydrogenation.

References:

1. *Angew. Chem. Int. Ed.* **2012**, 51, 1014–1018
2. *Tet. Lett.* **2012,** 53, 1025–1028

Keywords: *Asymmetric catalysis; Hydrogenation;*

Physical organic methods – I

O-084

SYSTEMS CHEMISTRY: CATALYSIS AND SELF-REPLICATION IN DYNAMIC MOLECULAR NETWORKS

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How the immense complexity of living organisms has arisen is one of the most intriguing questions in contemporary science. We have started to explore experimentally how organization and function can emerge from complex molecular networks.[1, 2] We focus on networks of molecules that can interconvert, to give mixtures that are can change their composition. Molecular recognition between molecules in such mixtures leads to their mutual stabilisation, which drives the synthesis of more of the privileged structures.[3, 4] We show for the first time how a substrate of a chemical reaction can induce the formation of a catalyst for this reaction. We also demonstrate how self-recognition can lead to self-replication.[5] We also show that the self-assembled structures can be covalently cross-linked through photo-initiated disulfide exchange, resulting the in the formation of hydrogels.[6]

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Keywords: *Supramolecular chemistry; Molecular recognition; Self-assembly; Macrocycles; Autocatalysis;*

Physical organic methods – I

O-085

NOVEL PHOTOCHROMIC SURFACTANT FOR ORGANIC REACTIONS IN AQUEOUS MEDIA

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With the concept of green chemistry and its twelve principles, organic chemists are strongly encouraged to use water as solvent in the largest number of synthetic steps. The reaction of water-insoluble substrates requires the use of molecules that can induce the transfert of reagent from organic solvent to water, or in a privileged way from air to the reactive aqueous mixture. Among those molecules, micelles or aggregates composed of amphiphilic moieties can be used. Numerous reports on the subject showed that surfactants have a significant effect on the yield and selectivity of the reactions studied.

Based on those results, the synthesis of a novel photochromic surfactant that can form aggregates reversibly in water was studied.[1] The main aim was the formation/disruption of aggregation by a simple UV irradiation, leading to the capture/release of the reagents or products. The targeted molecule obtained has a hydrophilic head derived from D-glucose, and a hydrophobic tail of alkyl type associated to an azobenzene chromophore. The hydrophilic and hydrophobic parts were clicked together.

To compare and test the properties of our system on a model reaction we chose the acetylation of anilines. Indeed, this reaction is an important and widely used transformation in organic synthesis and a number of reagents coupled with promoters or catalysts have been put forth. So our surfactant was used to allow the acetylation of amines in aqueous medium and the recycling of the media from experience to experience. The process was simply to release the acetamide formed thanks to a UV irradiation, to filtrate and purify the residue, and to carry out again another reaction in the filtrate medium collected.

The design, synthesis and physico-chemical studies will be detailed.

References:

1. Drillaud, N.; Banaszak-Leonard, E.; Pezron, I.; Len C. submitted to *Angew. Chem. Int. Ed.*

Keywords: *Photochromism; Surfactants; Azo compounds; Isomerization; Acylation;*

Physical organic methods – I

O-086

PHOTOINDUCED DYNAMICS IN A TERPYRIDINE-BASED ZINC(II) COORDINATION POLYMER AND THEIR MOLECULAR FRAGEMENTS

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[2] *Friedrich-Schiller-University Jena, Jena Center for Soft Matter, Jena, Germany*
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This contribution focuses on the photoinduced dynamics in a Zn^{II}-*bis*-terpyridine coordination polymer and its molecular fragments – in particular the *bis*-terpyridine ligands bearing conjugated chromophore units, which resemble the structural features of poly[2-methoxy-5-(2-ethylhexyloxy)--1,4-phenylenevinylene] (MEH-PPV). The Zn^{II} coordination polymer, which forms ridgid linear macromolecular structures, combines up to about 35 such individual MEH-PPV-like chromophores and is investigated by single molecule fluorescence spectroscopy. Upon incorporation of the individual chromophores into the coordination polymer the fluorescence quantum yield of an individual chromophore is found to be reduced. The molecular mechanism underlying this finding is addressed by investigating the brightness of isolated polymer molecules in various environments. The SMS results show that the Zn^{II}-*bis*-terpyridine coordination polymer with the MEH-PPV-like chromophore structure contains a significantly larger fraction of bright chromophores compared to MEH-PPV alone. This finding is attributed to the particularly rigid geometry of the system at hand. The single-molecule fluoresecence experiments will be correlated with ultrafast time-resolved spectroscopy pointing to the photoinduced geometrical rearrangement in the *bis*-terpyridine chromophores. Finally, experiments on the Zn^{II} coordination polymer under different atmospheric conditions offer further insights into the molecular mechanism and the nature of the quenchers involved in the blinking.

Acknowledgement: *Support by the Fonds der Chemischen Industrie is acknowledged.*

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Keywords: *Zn(II) coordination polymers; photophysics; terpyridine coordination compounds; excited-state dynamics; luminescence properties;*

Physical organic methods – I

O-087

FLUORESCENCE SPECTRA PREDICTION OF OLIGOTHIOPHENE DERIVATIVES: COLOR TUNING BY SUBSTITUENT VARIATION

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Organic electronics [1] has gained both academic and industrial interest during recent years. Especially organic light emitting devices (OLEDs) have drawn much attention on them, as they show superior properties, e.g. a higher viewing angle and lower power consumption when compared to their inorganic counterparts. Thus, tools assisting the efficient development of novel materials suitable for the fabrication of OLEDs are highly appreciated. Bis(triarylamine) substituted oligothiophenes,[2] often described as cap-linker-cap systems, are typical representatives for a whole class of OLED materials. Variation of conjugation length of the oligothiophene linker as well as the decoration of the triarylamine cap with different substituents R enable tuning of spectral properties. Aim of this study was to investigate the influence of the substituent R on the fluorescence characteristics. In order to have knowledge upon this critical property before time consuming synthesis, we evaluated the possibility to predict fluorescence spectra by means of computational chemistry. For this purpose time-dependent density functional theory (TDDFT) was used, giving in the first step information on the vertical emission, both in gas phase and in solution. To move one step further, vibrational information was used to get insight into the particular band shapes of the entire spectra. Simulations based on the Wigner distribution, as implemented in the framework of the Newton-X program package, proved to be appropriate to perform this task.[3] The hereby obtained spectra were compared to experimental data to show scope and limitation of the methods under investigation.

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Keywords: *Density functional calculations; Fluorescence; Sulfur heterocycles; Semiconductors;*

Physical organic methods – II

O-088

PROBING PROTON TRANSFER REACTIONS IN CATALYSIS: PHYSICAL ORGANIC TOOLS

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Proton transfer reactions are ubiquitous in chemical and biological processes, and are often key to efficient catalysis. We use a physical organic chemistry approach towards deciphering reaction mechanisms based on organic synthesis, reaction kinetics and structure-activity studies. This presentation will focus on the physical organic methodology that we use to probe the dynamics of proton transfer and for pK_a determination. In particular, the study of proton transfer at carbon is central to our research and recent results of the proton transfer reactions of N-heterocyclic carbenes will be used to showcase our methodology. Analysis of the kinetics of hydrogen/deuterium exchange at carbon has allowed us to access the kinetic and thermodynamic acidities of a broad range of conjugate acids of imidazol-2-ylidenes, imidazolin-2-ylidenes, trihydropyrimidin-2-ylidenes and triazol-3-ylidenes. Notably, p*D*-rate profiles for deuterium exchange reveal that protonation to give dicationic triazolium species occurs under acidic conditions, allowing the carbon acid pK_a values for the conjugate acid precursors to *cationic* triazol-3-ylidenes to be estimated. As a further illustration of the tools used to probe proton transfer, our recent studies of a range of key Bronsted acid and base organocatalysts will be outlined.

Keywords: *Acidity; Protonation; Isotopic labeling; organocatalysis; kinetics;*

Physical organic methods – II

O-089

SYNTHESIS AND DYNAMICS OF CRYSTALLINE POLYFUNCTIONAL CHIRAL ROTORS

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We present the synthesis and structures of a variety of amphidynamic solids based on symmetrically and dissymmetrically functionalised 1,4-Bis(ethynyl)bicyclo[2.2.2]octane (BCO) moieties. The stochastic rotational motion of the BCO helixes in the condensed phase is investigated by variable-temperature X-ray and ^{1}H spin-lattice relaxation. In addition the torsional motion that switches the right-left configuration of the three rotor blades is analysed and discussed in the context of the modulation of the electro-optical properties of the systems.

Keywords: *Ligand design; Metal-organic frameworks; NMR spectroscopy; X-ray diffraction; Nonlinear optics;*

Physical organic methods – II

O-090

TUNING OF TRANSPARANT SUBSTRATES: SELECTIVE ANTI-BIOFOULING AND/OR SPECIFIC CELL GROWTH ONTO ITO VIA ORGANIC MONOLAYERS.

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Covalently attached organic layers on indium tin oxide (ITO) surfaces can be prepared by the photochemical grafting with 1-alkenes. THis is relevant, since ITO is not only fully transparant, but also electrically conducting. By taking suitably substituted alkene substrates, a tailor-made and extremely mild functionalization of the surface can be obtained in one step!

The surface modification was monitored with static water contact angle, X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM) measurements. Hydrophobic methyl-terminated ITO surfaces can be obtained via the grafting of tetradec-1-ene, whereas the attachment of w-functionalized 1-alkenes leads to functionalized ITO surfaces. The use of a CΞC-Ge(CH3)3 terminus allows for facile tagging of the surface with an azido group via a one-pot deprotection/click reaction, resulting in bio/electronically active interfaces. The combination of non-aggressive chemicals (alkenes), mild reaction conditions (room temperature) and a light-induced grafting that facilitates the direct patterning of organic layers possible makes this simple approach highly promising for the development of ITO-based (bio) electronic devices. The presentation will outline the methodology and provide a detailed surface characterization to demonstrate the potential for local biofunctionalization of ITO with complex bio-organic moieties (reference 1).

In addition, it will outline current developments for the local attachment of functionalizable zwitterionic polymers that fully repel any protein deposition and cell growth of human colon (Caco-2) cells. The local deposition of the polymer layer can be used to enable the local cell growth on this transparant substrates onto uncoated or RDG-coated areas. In this manner, covalently attached polymeric layers (20 nm) can be used to direct patterned cell growth, and allow the construction of bio-electronic architectures.

References:

1. Li, Y.; Zuilhof, H. *Langmuir* **2012**, *28*, 5350–5359.

Keywords: *cell adhesion; monolayers; surface chemistry; photochemistry;*

Physical organic methods – III

O-091

EFFICIENT CATALYST REUSE BY DISSOLUTION IN NON-CONVENTIONAL MEDIA

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Efficient catalysis is an important topic in modern synthetic transformations and provides precious contribution for the development of more sustainable chemistry. However, generally due to the high cost of required rare metals and/or necessary considerable synthetic demand for the synthesis of many catalytic systems, is very important to achieve efficient methodologies for catalysts reuse without affecting the main features of the catalyst. The major approach to catalyst reuse is based on chemical immobilization of the catalyst in organic or inorganic support and under heterogeneous conditions which in many cases leads to some erosion of the catalytic system performance. On the other hand, the use of homogeneous conditions is in general more efficient but the catalyst reuse needs more elaborated approaches such as anchoring the catalyst on polymer with tunable solubility, incorporation of anchoring groups on the catalyst with high affinity to alternative reaction media such as fluorinated solvents/supports, PEG, supercritical CO_2, water and ionic liquids. Another simpler approach for catalyst reuse is based on the use of original catalytic system under homogeneous conditions and without any chemical manipulation just by appropriate choice of the reaction medium - separation process.[1]

In line with our contribution in this area,[2] here is described recent achievements from this laboratory on novel catalyzed transformations such as: **a**) Bronsted acid-catalyzed dihydroxylation of olefins in aqueous medium; **b**) Asymmetric Rh(II) carbenoid C-H insertion of alpha-diazo-acetamides and **c**) Production and isolation of 5-hydroxymethylfurfural(HMF) from carbohydrates.

Acknowledgment: *We would like to thank FCT and FEDER for financial support.*

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Keywords: *Asymmetric catalysis; Carbohydrates; Green chemistry; Insertion; Oxidation;*

Physical organic methods – III

O-092

MICROWAVE-ASSISTED CU(I)-CATALYZED COUPLING OF AMINES, ALDEHYDES AND ACETYLENES

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The three-component coupling of an amine, an aldehyde and an acetylene (A3-coupling) attracts attention of chemists for the last decade. Among other catalysts, Cu(I) salts proved to be the most efficient and economical catalysts. The outcome of the A3-coupling reaction depends on the nature of the starting compounds. For example, the coupling of primary amines with aldehydes and acetylens provides secondary propargylamines. The same reaction with propiolic acids leads to the trisubstituted oxazolidinones. We have also developed the decarboxylative A3-coupling reaction affording tertiary propargylamines. Finally, the Cu(I)-catalyzed decarboxylative A3-coupling using glyoxalic acid provided interesting aminoenynes.

References:

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Keywords: *A3-coupling; organic catalysis; propargylamines; microwave-assisted organic synthesis; copper catalyst;*

Physical organic methods – III

O-093

A SERIES OF BIS-TRIAZOLYL BENZOCHALCOGENDIAZOLE TRIMERS AND THEIR USE AS METAL ION SENSORS

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The prevalence of metal ions in the environment and their occurrence in biological systems has created a need for the detection and differentiation of such species. Spectrophotometric methods have emerged as a powerful tool for metal ion detection due to their simplicity, sensitivity, and versatility. Previously we reported on the metal-binding properties of bis-triazolyl heteroaromatic trimers, benzothiadiazole in particular. We have already shown that variation of the heteroatom from oxygen to sulfur to selenium affects the electronic properties of benzochalcogendiazoles; in this work we examine the effect of this structural variation on the metal-binding properties of their bis-triazolyl cycloadducts.

These fluorescent metal sensors were synthesized via 'click' coupling of an azide with the bis-ethynyl heteroaromatic core. Because aqueous solution is the ideal media for metal ion sensing, an azide with a water-soluble substituent was used. The branched oligo(ethylene glycol) substituent chosen provides excellent water-solubility and improved quantum yields.

The chalcogen atom in the heteroaromatic core of these sensors plays an important part in the electronic properties of the cycloadducts. Moving down the group from oxygen to selenium induces bathochromic shifts in the absorption and emission spectra. Selenium shows the largest effect on the photophysical properties; the oxo- and thiadiazole click products are both green-fluorescent, while the seleno- congener fluoresces orange.

The effect of the heteroatom on the metal-binding properties was also investigated. Binding constants of different metals were determined from the fluorescence quenching response. The click product containing the more electronegative oxygen atom showed very weak metal ion binding. The counterparts containing sulfur and selenium were able to efficiently bind Ag(I), Cu(II), and Ni(II) ions. The fluorophore containing selenium, the largest and least electronegative atom, displayed the strongest binding. Additionally, the absorbance response pattern of these fluorophores is different for each metal, allowing differentiation of copper, silver, and nickel.

Keywords: *nitrogen heterocycles; fluorescent probes; fluorescence spectroscopy; click chemistry;*

Physical organic methods – III

O-094

MICROWAVES AND MULTI-COMPONENT REACTIONS IN THE SYNTHESIS OF MEDIUM-SIZED RINGS

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Medium-sized rings are abundantly present in many biologically active (natural) products as e.g. the alkaloids aphanorphine, lennoxamine and cephalotaxine and the noncompetitive *N*-methyl-D-aspartate (NMDA) receptor antagonist Dizocilpine, also known as MK-801. However, the synthesis of medium-sized rings is known to be rather cumbersome and no good generally applicable procedures have been described so far. Some time ago we have elaborated an efficient synthesis of the 3-benzazepine framework via an intramolecular Heck reductive cyclization. We have demonstrated that the application of microwave irradiation is beneficial for this process. As a result of these investigations we extended our research towards the synthesis of indoloazocines, dibenzoazocines, dibenzoazepines, 3-benzazepines and dibenzo[c,e]azepinones. To assure the generation of diversity we utilized multicomponent reactions as the aldehyde/amine/alkyne (A3) coupling and the Ugi 4CR which will be run in an intramolecular fashion. The beneficial effect of the application of microwave irradiation in each of these processes will be commented.

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Keywords: *Microwave chemistry; Medium-ring compounds; Multi-component reactions;*

Physical organic methods – III

O-095

PHOSPHORESCENT IRIDIUM COMPLEXES CONJUGATED TO CXCR4-TARGETING PEPTIDES FOR LIFETIME IMAGING

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Fluorescence lifetime imaging microscopy (FLIM) is an optical imaging technique that produces contrast based on differences in luminescence decay rates (lifetime). Standard organic dyes such as fluorescein generally have lifetimes of < 10 ns, which is also the case for autofluorescence generated by cells and tissue. On the other hand, transition metal complexes possess lifetimes of > 100 ns, which makes discrimination from autofluorescence unambiguous. To benefit from these long lifetimes in targeted imaging applications, we have prepared phosphorescent iridium(III) complexes for chemokine receptor 4 (CXCR4) targeting. CXCR4 over-expression is found in many types of cancer, where it plays a role in, among others, the metastatic spread. For this reason it is an interesting biomarker for the field of molecular imaging.[1]

Three iridium complexes, containing one, two or three β-alanine spacers, were synthesized.[2] They had luminescent lifetimes of 200-220 ns, absorption maxima of approximately 400 nm and emission maxima of approximately 570 nm. The iridium complexes were functionalized with one, two or three targeting peptides to allow for CXCR4 visualization. The CXCR4 receptor affinities of the mono-, di- and trimeric peptide derivatives were determined using flow cytometry and amount 84.4, 254.4 and 66.3 nM, respectively. All three derivatives did not cause cytotoxicity up to 3 μM concentrations and could distinguish between cell lines with different CXCR4 expression levels. FLIM showed that the peptide–iridium complex conjugates can be used to visualize CXCR4 expression in tumor cells with very high contrast.[3]

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Keywords: *Luminescence; Metal-organic frameworks; Peptides; Fluorescence spectroscopy; Synthesis design;*

Polymer chemistry – I

O-221

MULTICOMPARTMENT MICELLES FROM MULTIBLOCK MULTICOMPONENT POLYMERS IN SELECTIVE SOLVENTS

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Controlled formation of compartmentalized spherical micelles with self-assembled complex hierarchical structures was demonstrated by using linear and non-linear multiblock multicomponent polymers {ABCD, ABCED, and $(ABC)_2D$, where A:polystyrene; B:polyisoprene-1,4; C:poly(dimethylsiloxane); D:poly(2-vinylpyridine) and E:poly(tert-butylmethacrylate)} in selective solvents. These tetrablock *quarter* and pentablock *quinto* polymers were synthesized by using anionic polymerization high vacuum techniques and appropriate chlorosilane-based heterofunctional linking agents. The molecular characteristics of the multiblock multicomponent polymers were obtained by osmometry, light scattering, size exclusion chromatography (SEC) and NMR. The multicompartment character of the micellar aggregates was studied by Static/Dynamic Light Scattering (SLS/DLS), Transmission Electron Microscopy (TEM/Tomography), and Atomic Force Microscopy (AFM). Using suitable solvent systems we have constructed well-defined micellar hierarchies with collapsed unprecedented tri-componential core and compartmentalized or mixed corona. The ratio of the different blocks in the core and corona was varied by the quality of the solvents and solvent mixtures used in the experiments.

Keywords: *multiblock multicomponent copolymers; selective solvents; multicompartment micelles; transmission electron microscopy; static/dynamic light scattering;*

Polymer chemistry – I

O-222

CRYSTALLINE PROPERTIES OF PVAC-B-PCL BLOCK COPOLYMERS: INFLUENCE OF THE SYNTHESIS ROUTE

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Poly(vinyl acetate)/poly(ε-caprolaclone) block copolymers (PVAc-b-PCL) were synthesized using two different approaches: a “coupling reaction” approach and a “macroinitiator” one. For the coupling approach, a chain transfer agent, with an azide function, was used to initiate the polymerization of VAc. PCL containing an alkyne termination was also prepared. These two reaction products, PVAc and PCL, were then coupled by a click chemistry reaction to obtain the corresponding block copolymer. For the macroinitiator approach, PCL-b-PVAc block copolymers were obtained by a two-step procedure: first, a macroinitiator PCL with a xanthate end group was prepared, then, the polymerization of VAc was initiated by RAFT polymerization from the PCL, allowing to obtain PVAC-b-PCL block copolymers. Different copolymers, varying by their blocks lengths, were prepared with both methods. Elsewhere, PCL is a semi-crystalline polymer, and consequently, PCL blocks of PVAc-b-PCL are able to crystallize.The objective of this work is then to analyse the influence of the synthesis way of copolymers on the crystallinity of PCL blocks. Crystalline properties have been investigated by differential scanning calorimetry (DSC).

The results indicate a decrease of the crystallinity of the PCL block in copolymers obtained by the “coupling” method, compared to PCL homopolymers, contrary to copolymers obtained through the “macroinitiator” approach for which the crystallinity of the PCL was much less affected. This influence of the synthesis method was explained by the presence, in the copolymers obtained by click reaction, of a rigid triazol cycle (cycle binding the two blocks of polymer). This triazol cycle limit the relative mobility of the two blocks and decrease the possibility of organization and the crystal formation. This study has evidenced the great influence of the synthesis route on copolymers crystallinity and the major effect of the presence of the triazol cycle, inducing a high decrease of the crystallinity degree

Keywords: *Crystal growth; Polymers; Calorimetry;*

Polymer chemistry – I

O-223

SULFONATION OF POLYBUTADIENE AND BUTADIENE-STYRENE COPOLYMERS AS VERSATILE ROUTE FOR THE PRODUCTION OF POLYELECTROLYTES AND IONOMERS WITH ENHANCED THERMAL STABILITY AND CONTROLLED MORPHOLOGY

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Sulfonated ionomers find applications ranging from ion exchange membranes for fuel cells to superacid catalysts, surfactants, compatibilizers and sensors. Typical examples are sulfonated polystyrene, polybenzimidazole and polyphenylene oxide in which the sulfonic acid groups are randomly introduced onto the aromatic rings of the polymer chains. The selective functionalization of polymer segments in block copolymers is more challenging but of interest for the production of phase separated materials containing polar domains homogeneously dispersed in hard polymer matrices.

In this presentation we describe a two steps process which allows the fast and selective sulfonation of olefinic carbon-carbon double bonds of polybutadiene and polystyrene-*b*-polybutadiene-*b*-polystyrene triblock copolymers (SBS), without producing crosslinking of the polymer chains and functionalization of aryl groups. High level of sulfonation and ion exchange capacities (IEC) were thus obtained. Sulfonation of semicrystalline multiblock syndiotactic polystyrene-*co*-*cis*-1,4-polybutadiene (**sPSB**)[1] led to**sPSB-SA** in which the polybutadiene segments are completely sulfonated and the crystallinity of the syndiotactic polystyrene domains is preserved. A thin film by spin-coating of **sPSB-SA (**12 *mol*% of -SO_3H) showed at AFM analysis a phase separated morphology, consisting of conductive regions of few tens of nanometers embedded in a non conductive matrix of syndiotactic polystyrene. The thermal stability of **sPSB-SAs** was investigated by DSC and TGA-FTIR analysis. **sPSB-SA** samples debated in water/chloroform solvent mixture produced micelles of 200-300 nm highlighted by TEM analysis. The selective staining with Pb(II) revealed the core-shell nature of the micelles, exhibiting -SO_3H groups on the surface.

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Keywords: *sulfonation; polyanion; Nanostructures; Block copolymers;*

Polymer chemistry – I

O-224

AMPHIPHILIC CATIONIC CARBOSILANE-PEG DENDRIMERS: SYNTHESIS AND APPLICATIONS IN GENE THERAPY

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The interest on treating diseases by gene therapy has clearly bloomed as consequence of the increase knowledge on disease molecular pathways and human genome. This method requires guiding functional genetic material (plasmids, nucleic acids, oligonucleotides) to the target cells.[1] Macromolecules, polymers and nanosystems, which can be rationally designed, have been employed as synthetic gene vectors. These vectors have to interact with the nucleic acids, usually forming electrostatic complexes compacting them and preventing their degradation. Thus, different systems functionalized with cationic groups have been employed for this objective. In the particular case of dendritic macromolecules, their properties such as well defined size and structure, flexibility, monodispersity and multivalency molecular surface have attracted attention for biomedical applications.[2]

Carbosilane dendrimers present a hydrophobic framework. The introduction of ammonium groups at the periphery turn them water soluble and have been successfully tested as gene transfer agents.[3] However, the major drawback of cationic dendrimers is their intrinsic toxicity. An adequate procedure to overcome this problem has been PEGylation of these systems, increasing also the solubility of the macromolecule.[4]

We described here the synthesis of cationic amphiphilic carbosilane-PEG dendrimers with ammonium groups *via* click chemistry coupling of carbosilane (generation 1 to 3) and PEG-based dendrons functionalized at the periphery with NHBoc groups. The cationic heterodendrimers thus obtained have been evaluated in gene therapy against HIV in Peripheral Blood Mononuclear Cells, and their results compared with a carbosilane homodendrimer.

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Keywords: *Dendrimers; Antiviral agents; Amphiphiles; Cations;*

Polymer chemistry – II

O-225

PHOTO, ELECTRO, BIO AND THERMALLY FUNCTIONAL POLYMERS BY CLICK CHEMISTRY

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Recently, 1,3-dipolar cycloadditions, from the reactions between azides and alkynes or nitriles, known as ‘click reaction have been recognized as a useful synthetic methodology and applied to macromolecular chemistry offering materials ranging from the block copolymers to the complex macromolecular structures. These cycloaddition reactions enabled the C-C bond formation in a quantitative yield without side reactions and requirement for additional purification steps. The click reactions are particularly important in preparative methods, in which high conversion of functional groups is desirable. Numerous applications of Click chemistry in polymer science as well as molecular biology and nanoelectronics have recently been reviewed. In recent years, several other click reactions based on Diels-Alder cycloaddtion, thiol-ene chemistry and keten chemistry have been proposed.

In this presentation, various click reactions, namely 1,3-dipolar cycloadditions, Diels-Alder cycloaddition, thiol-ene chemistry and keten chemistry for the preparation of block and graft copolymers, and polymers possessing electro, bio, photo and thermo active groups will be presented. Moreover, several new photo-induced click reactions developed in author’s laboratory will be addressed.

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Keywords: *click chemistry; polymers; biological activity; photochemistry; electrochemistry;*

Polymer chemistry – II

O-226

CATALYSTS IMMOBILIZATION: A SIMPLE AND EFFICIENT TOOL TO ENFORCE STEREOSELECTIVE PRODUCTION OF COMMODITY AND BIODEGRADABLE POLYMERS

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Commodity polymers such as polymethylmethacrylate or polydienes are ubiquitous in everyday life. On the other hand, biodegradable polymers such as aliphatic polyesters are attracting an ever growing attention, as potential answers to key environmental issues. They can be accessed by lactone ring-opening polymerization using rare-earth metal initiators. The polymers mechanical properties are chiefly governed by their microstructure, which in turn can be controlled through catalyst design, using ligands derived from multistep synthesis.[1] A simple way to produce stereoselective catalysts without time-consuming synthetic procedures is therefore of considerable interest.

This problem can be efficiently tackled by use of well-defined supported catalytic systems based on rare-earth metal species.[2] Indeed, in sharp contrast to their homoleptic molecular counterparts, immobilized derivatives provide polymers with high degree of stereocontrol.[3] This has been shown for several monomers (methylmethacrylate, isoprene, styrene, *beta*-butyrolactone). We will show that this is linked to the grafting chemistry, by determining structure-selectivity relationships: a precise control over the surface species structure is of prime importance. Furthermore, understanding of this beneficial “surface effect” has been addressed through DFT calculations, which clearly demonstrate the impact of the silica surface on successive stereoselective monomer enchainments.[4]

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Keywords: *Ring-opening polymerization; Rare Earths; Supported catalysts; Polymerization; Density functional calculations;*

Polymer chemistry – II

O-526

PERFLUORINATED AMPHIPOLAR POLYMERS AT INTERFACES

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Surface active compounds play a decisive role for various applications. While in most cases one focuses on hydrophilic/hydrophobic structures herein the use of perfluorinated amphiphiles is discussed. In three different examples, it is demonstrated that these molecules are very powerful surface active compounds. Their synthesis and application is highlighted and described in regard to adjusting liquid-liquid and solid-liquid interactions: In particular, (**i**) fluorous amphiphilic block copolymers were designed to stabilize nonaqueous emulsions even suitable for metallocene catalyzed polymerisations, (**ii**) statistical copolymers were utilized to functionalize and compatibilize the surface of inorganic nanoparticles, and finally (**iii**) terpolymers were applied to obtain superhydrophobic properties.

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Polymer chemistry – III

O-227

SYNTHESIS AS KEY TOWARDS IMPROVED (OPTO)ELECTRONIC MATERIALS

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The lecture presents recent synthesis driven approaches towards systematic control on morphology and (opto)electronic properties of conjugated oligomers and (co)polymers. The examples include conjugated (co)polymers for application in organic solar cells,[1 2] all-conjugated rod-rod block copolymers and their self-assembly in solvent mixtures and in the bulk,[1,3-5] as well as hyperbranched, multichromophoric conjugated polymers.[6]

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Keywords: *Conducting materials; Polymers; Semiconductors; Block copolymers; Amphiphiles;*

Polymer chemistry – III

O-228

SURFACE FUNCTIONALIZED POLYPHENYLENE DENDRIMERS

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Modifying the periphery of dendrimers affects properties such as solubility, aggregation and membrane penetration. A new type of amphiphilicity on the periphery of polyphenylene dendrimers (PPDs) is investigated by designing the periphery in an unprecedented way and scale. Polar (sulfonic acids) and non-polar groups (alkyl chains) were placed alternating close to each other on a sub-nanometer length scale (7?) to create small hydrophilic and hydrophobic domains on the surface.

While in case of amphiphilic nanoparticles the surface patterning relies on self-assembly, dendrimer synthesis allows the right placement of different functional groups at assigned positions. Thus the number and arrangement of functional groups as well as the distance between them can be adjusted. Backward folding of the periphery into the dendrimer interior is prevented by the rigid PPD scaffold so that functional groups of different polarity are fixed on the surface. Polarity differences lead to a permanent repulsion between the different functional groups. These functional groups cannot rearrange into a fully phase segregated state due to their fixed positions. This frustration leads to unique solubility i.e in polar and non-polar solvents as well. An application of such an amphiphilic PPDs as a transport agent for phase transfer (i.e. drug delivery via membranes) is presently being investigated.

On the other hand two polyphenylenedendrons of different polarity can be combined to a so called "JANUS"-dendrimer. Such type of a PPD containing a hydrophilic and a lipophilic hemisphere should form supramolecular structures due to their strong aggregation.

Furthermore, the switchability of the surface polarity and thereby the solubility is enabled by the incorporation of photoswitchable azobenzenes in the scaffold of our PPDs is under investigation. We aim to be able to switch the solubility in polar solvents on and off by light.

Keywords: *Dendrimers; Amphiphiles;*

Polymer chemistry – III

O-229

NEW LOW ENERGY GAP POLYMERS FOR APPLICATION IN SOLAR CELLS

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Research into the use of conjugated polymers for application in bulk heterojunction solar cells has been the subject of much interest in recent years in view of their potential technological value for energy generation. Major advances have been achieved in this area; however, new polymer systems with high absorption coefficients and extended absorption spectra are still being sought for use in this area.

The design of low energy-gap conjugated polymers can be achieved by introduction of alternate electron donor and acceptor repeat units along the polymer chains which results in intra-molecular charge transfer. This approach proved successful in the preparation of a range of narrow energy gap polymers for application in bulk heterojunction solar cells. Donor/acceptor systems comprising copolymers with alternating 2,7-carbazole repeat units along with acceptor repeat units have been described by Leclerc et al. and showed great promise when used with PCBM in bulk heterojunction photovoltaic cells with good power conversion efficiencies. We have reported recently the preparation of a series of donor / acceptor alternating copolymers comprising dithienyl benzothiadiazole with alkoxy substituents and 2,7-linked carbazole repeat units. The polymers showed higher open circuit voltage (V_{oc}) values than that of **PCDTBT** and good power conversion efficiencies with PCE values of 4.22 and 4.12%.

In this work, we report the preparation and characterization of new classes of low energy gap donor/acceptor alternating copolymers, comprising 2,7-linked carbazole repeat units and alternate repeat units including selenophenyl benzo[1,2,5]thiadiazole units and thienothiophenyl benzo[1,2,5]thiadiazole units. We also present studies on the physical properties of the polymers and their ability to act as electron donors to PCBM as well as their performance in bulk heterojunction solar cells in blends with PCBM.

Keywords: *Conjugated polymers; Organic photovoltaics; Bulk heterojunction solar cells;*

Polymer chemistry – III

O-230

SELF-HEALING POLYMER COATINGS BASED ON THE (RETRO) DIELS-ALDER REACTION

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Self-healing materials feature the extraordinary property that a damage inflicted to them can be healed (partially or completely). Hereby the original function of the material can be restored. In Nature this process is very common: a cut in the finger can be healed, broken bones merge,...

However, man-made materials very often lack this special ability. In contrast to natural materials they were designed in order to prevent the damage, not to manage and handle damage, which will inescapable occur during usage of common materials. Self-healing coatings are of particular interest, because coatings are very prone to damage. Latter will lead to a loss of the function of the coating: protection of the underlying material and aesthetical exterior.

Self-healing can be achieved in coatings by extrinsic materials, i.e. a healing agent is embedded into the coating (e.g., within capsules). In addition, the polymeric material of the coating itself can feature the ability for healing. In this context, we report the synthesis of novel acrylic polymers, which contain both binding units for the Diels-Alder reaction (i.e. the maleimide and the furan moiety). The ATRP was utilized to synthesize well-defined functional terpolymers, which could be crosslinked via thermal treatment. Different comonomers have been utilized to tune the thermal and mechanical properties of the resulting polymer networks.

Moreover, the healing of scratches in polymer coatings, based on these materials, was investigated. The influence of the crosslinking density, the kind of the comonomer and the healing temperature on the ability for self-healing was investigated in detail. Efficient healing of polymer coatings could be obtained.

Keywords: *Polymers; Materials science; Cycloaddition; Pericyclic reaction;*

Polymer chemistry – III

O-231

DESIGN AND SYNTHESIS OF NOVEL SERINE BASED GEMINI SURFACTANTS: HOW DOES STRUCTURAL MODIFICATION AFFECT MICELLIZATION AND CYTOTOXICITY

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Gemini surfactants represent a new generation of compounds composed of two surfactant monomers linked chemically at or near the head groups by a rigid or flexible spacer. Owing to their excellent performance and enhanced physicochemical and biological properties in comparison to the corresponding monomeric counterparts, gemini surfactants have a broad range of applications, ranging from cosmetic and food formulations, models for membranes and microreactors, to drug and gene delivery systems, among others.[1] Therefore, considerable efforts have been made to design and synthesize new forms of gemini surfactants, focusing on the effect of the nature of the polar head group and of the spacer length and hydrophobicity on the aggregation properties as well as on the toxicological profile of the compounds.

In this context, our research group has been engaged in the synthesis and evaluation of the basic physicochemical properties of amino acid based monomeric and dimeric surfactants.[2] In the present work, the results obtained with two novel series of cationic gemini surfactants based on serine are presented. The most efficient synthetic pathway was established and involves the introduction of the spacer into the *N*, *N*-dialkylated monomeric precursors by peptide condensation methods, subsequent methylation and deprotection. The final target surfactants have either an amide or an ester bond between the polar head group and the spacer. These surfactants showed enhanced micellization properties compared to the conventional bis-quats. A study on the influence of the nature of the spacer linkage as well as of the spacer chain length has been performed. The cytotoxicity of the compounds has also been evaluated.

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Keywords: *surfactants; synthesis; cytotoxicity; self-assembly; amino acids;*

Polymer chemistry – IV

O-375

POLYMERIZATION-INDUCED SELF-ASSEMBLY OF AMPHIPHILIC BLOCK COPOLYMERS IN WATER

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The presentation will describe the formation of amphiphilic block polymer nanoparticles in water via an *in situ* process based on polymerization-induced self-assembly. This method relies on the employment of a hydrophilic living polymer precursor prepared via controlled free-radical polymerization that is extended with a hydrophobic second block in an aqueous or hydroalcoholic environment. The process thus leads to amphiphilic block copolymers that self-assemble *in situ* into self-stabilized nano-objects in the frame of an emulsion or dispersion polymerization process. Depending on the nature and the structure of the so-formed copolymer, not only spherical particles can be achieved but also all morphologies that can be found in the phase diagram of an amphiphilic block copolymer in a selective solvent. The presentation will focus mainly on the RAFT (reversible addition-fragmentation chain transfer) controlled free-radical polymerization technique using various hydrophilic and hydrophobic comonomers.

Keywords: *self-assembly; amphiphilic block copolymer; controlled-radical polymerization; reversible addition-fragmentation chain transfer; polymerization in dispersed systems;*

Polymer chemistry – IV

O-376

SYNTHESIS AND CONTROLLED IMMOBILIZATION OF AMPHIPHILIC BLOCK COPOLYMERS ON SOLID SUPPORTS

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Functionalization of surfaces using biomimetic block copolymer membranes enhances the development of smart surfaces for biotechnological applications that include biosensing and the local production and release of drugs. Instead of lipid membranes, amphiphilic block copolymer membranes have been chosen as mimics of biological membranes, due to properties such as tunable thickness, chemical and mechanical stability, lower permeability, fluidity, mobility, etc. Upon insertion of membrane proteins, these systems could allow for the preparation of mechanically and chemically robust, air-stable biosensing and drug delivery devices.

Surface-initiated atom transfer radical polymerization (ATRP) was used because it provides good control of brush thickness by controlling polymer molecular weight. Poly(2-hydroxyethyl methacrylate)-*block*-poly(n-butyl methacrylate)-*block*-poly(2-hydroxyethyl methacrylate), PHEMA-*b*-PBMA-*b*-PHEMA block copolymers were synthesized with the first PHEMA block anchored to a self-assembled monolayer of initiators on a gold surface, while the other PHEMA block was exposed to the outside. To achieve this, a self-assembled monolayer of $(BrC\text{-}(CH_3)_2COO(CH_2)_{11}S)_2)$ initiator was formed by disulphide ? gold covalent bonding.

The formation of the self-assembled monolayer was successfully characterized by AFM, contact angle- and X-ray photoelectron spectroscopy (XPS), providing information on the presence of chemical elements and their binding energies, and therefore on the structure of the initiator on the surface. Contact angle, ATR-FTIR, and AFM measurements were taken to monitor the ATRP synthesis. PHEMA brushes render the surface smoother and more hydrophilic, whereas PBMA brushes result in a rougher, more hydrophobic surface. The thickness was measured layer by layer by surface plasmon resonance (SPR), with an overall thickness of 39 nm.

ATRP was successfully applied to the grafting of ABA-triblock copolymer membranes from gold supports. Polymer brushes such as these, exhibiting a hydrophilic-hydrophobic-hydrophilic sequence, could be regarded as the first example of solid supported, biomimetic block copolymer membranes prepared by a "grafting-from" approach.

Keywords: *Biosensors; Block copolymers; Surface chemistry; Membrane proteins;*

Polymer chemistry – IV

O-377

NEW PDMS-B-PCL AND PCL-B-PDMS-B-PCL BLOCK COPOLYMERS FOR SURFACE NANO AND MICRO-PATTERNING

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Polydimethylsiloxane (PDMS) are particularly interesting polymers due to their broad combination of desirable properties as a low glass transition temperature (-120 °C), a high chain flexibility, a high resistance to chemical oxidation, high thermal and UV stability, a very pronounced hydrophobic character, as well as high biocompatibility. However, silicone polymers have so far been little used for the control of chemical modification of surfaces due to a strong dewetting tendency during adsorption on solid surfaces. To increase the chemical compatibility and promote irreversible adsorption, the synthesis of new block copolymers with a viscoelastic PDMS block was investigated. More precisely PDMS was copolymerized with e-caprolactone (e-CL) that is currently reconsidered with particular attention because of its biodegradability when polymerized.

The purpose of this study is to create micro-patterned surfaces with specific and adjustable properties (hydrophobic vs hydrophilic or rigid vs soft). Several block copolymers were synthesized by reacting hydroxy-functional PDMS oligomers with e-caprolactone. The synthesis of block copolymers AB and ABA were made by anionic coordinated polymerization. A wide range of combinations of well-defined diblock PDMS-b-PCL and tribloks PCL-b-PDMS-b-PCL copolymers were obtained. The molecular weights of block copolymers synthesized were determined by 1H NMR and SEC. The thermal and structural properties of copolymers were determined by DSC and FTIR spectroscopy. The structure of copolymers in the adsorbed state was studied by Atomic Force Microscopy (AFM) to reveal the impact of block copolymer microstructure on the micro-patterning properties.

The results show that the surface morphology of the adsorbed copolymer films can be tuned by the copolymer microstructure. In particular, the adsorption on a hydrophobic surface allows obtaining a 2D “porous” surface, for which the size of “cells” is determined by the microstructure of the copolymer.

Keywords: *Block copolymers; Polydimethylsiloxane; Polycaprolactone; Adsorption; Surface patterning;*

Polymer chemistry – IV

O-378

CHITOSAN-BASED LEATHER FUNCTIONAL COATINGS WITH IMPROVED ANTIMICROBIAL PROPERTIES

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Among the interesting biological activities that have been ascribed to chitosan, the antimicrobial activity is probably the one that generates the higher number of applications. Developing antimicrobial coatings for footwear components to be used in direct contact with the feet is of great interest; both at industrial level (reducing the possibility of material deterioration and quality loss) and from the consumer’s point of view (decreasing skin infections and minimizing unpleasant odours). One weakness of this application is addressed to the durability and efficiency of the product antimicrobial activity, since it is directly associated with the availability of the positively charged R–NH_3^+ groups that are depleted during use.

In this work chitosan-based microparticles loaded with limonene as a model core material have been produced using an atomization technique followed by a coagulation step with sodium tripolyphosphate solution and a finishing step with glutaraldehyde. By using microencapsulation it is expected that the loaded essential oil will progressively release, reinforcing the antimicrobial durability and effectiveness of the developed coating. Moreover, the empty chitosan carriers can act as an additional source of chitosan.

The chitosan-based microparticles were applied conjunctly with a chitosan solution (1% w/v in diluted formic acid solution) in a pilot scale drum during 2 hour at 50 ºC. The used leather samples correspond to half a hide arising from the industrial dye fixation stage split in two parts. After the coating process, the leather was dried in industrial conditions and stored in closed plastic bags before testing. The antimicrobial activity was tested using a Standard Test Method under Dynamic Contact Conditions based on the ASTM Standard E 2149-01. Comparatively to the leather impregnated with the base chitosan solution, the coatings reinforced with chitosan microparticles evidenced an improved antimicrobial activity.

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Keywords: *polymers; biological activity; natural products;*

Supramolecular Chemistry – I

O-379

CHIRAL CAPSULES WITH REVERSED POLARITY

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Molecule-sized synthetic container molecules (capsules and cavitands) have been of continuing interest to many researchers because they provide a specific, confined nanospace as a site for recognition and catalysis. Their unique constrictive internal environment and ability to eliminate solvent's influence have been sown to cause stabilization of unusual conformations, transition states and reaction intermediates. These features can be exploited for the construction of selective sensors, gas storage media and reaction nanovessels.

Most of the currently known synthetic container molecules (capsules and cavitands) have walls composed of aromatic rings. Therefore they have smooth and hydrophobic interiors incapable of directional interactions with guests, recognition of polar guests, distinguishing of enantiomers, performing in asymmetric reactions or generation of unidirectional motion. Their nonpolar interiors are also disadvantageous for catalytic purposes. Synthetic container molecules with chiral, polar walls capable of directional interactions with guests can potentially overcome these drawbacks and therefore are of great interest.

We have succeeded in the synthesis of a series of capsular dimers with hydrophobic outer surfaces and polar and chiral interiors. High kinetic stability of the resulting polar capsules requires a non-covalent approach to the synthesis and isolation. We will discuss various aspects of supramolecular synthesis of the polar capsules, involving reversible formation, self- and nonself-sorting and denaturation. We will also show their applications and use for basic research. For example: **a**) extraction and encapsulation of biologically relevant polar molecules from water phase; **b**) differentiation of enantiomers with detailed interaction studies based on X-ray analysis; **c**)model studies on the influence of water molecules on recognition and **d**) model studies on the guests' dynamics in restricted polar environment.

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Keywords: *Self-assembly; NMR spectroscopy; Calixarenes; Cavitands; Chirality;*

Supramolecular Chemistry – I

O-380

CHIRAL SUPRAMOLECULAR ORGANIZATION OF OLIGO(PHENYLENE ETHYNYLENE) (OPE)-BASED DISCOTICS: INDUCTION OF HELICITY AND AMPLIFICATION OF CHIRALITY

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The self-assembly of relative small molecules to yield supramolecular polymers is a matter of interest because the well defined and organized supramolecular structures can find applicability in material and biological science.[1] Many of these supramolecular structures exhibit a preferred handedness due to the incorporation of stereocenters at the peripheral substituents.

Here in we describe the self-aggregation of two series of triangular shape OPEs discotics.[2] One of them is composed by OPE-based trisamides with a variable number of chiral side chains that self-assemble following a cooperative mechanism into α-helices. The presence of only one stereogenic center is enough in this series to achieve a helical organization with a preferred handedness. However, the ability to amplify the chirality decreases upon decreasing the number of stereocenters. In the other series the amide functionalities are replaced by ether linkages which impedes the α-helical columnar organization, and no dichroic response is observed.

The amplification of chirality experienced by mixing some components of the two series has been studied. Thus, while the mixture of a chiral trisamide with chiral but non helical OPEs functionalized with 2 or 3 ether linkages does not result in an amplification of chirality, the combination of an achiral trisamide with a chiral but nonhelical bisamide-monoether OPE generates helical structures with a preferred handedness. These studies represent one of the scarce examples in which chirality is obtained from the formation of host-guest complexes between structurally analogous species that separately are CD-silent.

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Keywords: *Supramolecular chemistry; Self-assembly; Chirality; Hydrogen bonds; Helical structures;*

Supramolecular Chemistry – I

O-381

PEPTIDE NUCLEIC ACIDS (PNA) BEARING C5-MODIFIED URACIL DERIVATIVES: HIGHLY SELECTIVE PROBES COMBINING STACKING INTERACTIONS AND BASE PAIRING

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Peptide nucleic acids (PNA) are among the best performing molecules in the recognition of DNA and RNA, and are very useful in the development of diagnostic as well as therapeutic tools.[1, 2] In the present communication we describe the synthesis of PNA probes containing monomers bearing uracil bases modified at the C5 carbon. The pendant groups were designed to allow to maintain the usual Watson-Crick base pairing and to provide additional stacking interactions (pyrene or naphthalene units), additional hydrogen bonds (Hoogsteen-like, through linking of a second uracil group) or both. Building blocks for the C5 modified monomers were isoorotic acid (5-carboxyuracil) or 5-(azidomethyl)uracil. In the former case the preformed modified PNA monomer was produced, whereas for the latter the strategy of introducing pendant groups directly on the solid phase, during or after the PNA synthesis, was also used.

PNA thus synthesized bearing several pyrene units distributed along the chain showed remarkable recognition properties, due to the stabilizing effect of stacking interaction which allowed to form stable triplex structures. The occurrence of these interactions was probed by excimer band formation in the emission spectrum, which was highly sequence selective. Thus these type of derivatives turned out to be excellent fluorescent probes for the target point mutation on DNA.

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Keywords: *Peptide Nucleic Acid; Uracil derivatives; Stacking interactions; Modified Nucleobases; Fluorescent probes;*

Supramolecular Chemistry – II

O-382

FOLDAMERS: EXPANDING THE CHEMICAL SPACE

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Our group has developed helical foldamers – oligomers that adopt stable helical folded conformations – derived from aromatic amino acids.[1] Some of these folded objects have shown unprecedented conformational stability,[2] and constitute convenient building blocks to elaborate synthetic, very large (protein-sized) folded architectures.[3] They possess a high propensity to assemble into double, triple and quadruple helices.[4] Cavities can be designed within such synthetic molecules that enable them to act as artificial receptors[5] and molecular motors.[6] Water soluble analogues of these foldamers show promise in nucleic acid recognition.[7]

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Keywords: *Supramolecular Chemistry;*

Supramolecular Chemistry – II

O-383

SUPRAMOLECULAR NUCLEIC ACID STRUCTURES FOR NANOMEDICINE AND DIAGNOSTICS

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Chimeras of DNA and different other synthetic materials like polymers, catalysts and dyes have gained increasing importance in recent years due to their ability to form functional supramolecular nanostructures in a modular fashion by employing Watson-Crick base pairing.[1] First, the combination of DNA and synthetic macromolecules will be discussed. Amphiphilic linear DNA block copolymers (DBCs) undergo microphase separation and form micelle aggregates in aqueous solution and their structural properties can be manipulated by hybridization.[2] Moreover, the organization of DBCs in liposomes and nanoelectronic devices will be demonstrated.[3] In the context of applications, the uptake of DNA block copolymer aggregates with different shapes into cells was studied. Based on these results their use as combinatorial platform for drug delivery was realized.[4]

Furthermore, oligonucleotides were conjugated to dyes containing a heavy atom like iodine that induces quenching of the photoluminescence. When employed in a DNA-templated Heck-reaction the fluorescence signal was restored allowing DNA detection.[5]A strongly amplified detection system was realized by DNA-directed assembly of a dehalogenation catalyst resulting in a detection limit of only 10 fM.

Finally, non-covalent complexes of nucleic acids with structurally complex natural products will be highlighted. The RNA supramolecular protective groups block several functionalities in an antibiotic bearing several chemically equivalent groups and enable the highly chemo- and regioselective derivatization of drug molecules in a single synthetic step. This technology will dramatically accelerate the drug development process avoiding costly and cumbersome synthetic routes.

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Keywords: *DNA; block copolymers; drug delivery; sensing; catalyst;*

Supramolecular Chemistry – II

O-384

BUILDING SYNTHETIC AND THERAPEUTIC PROTEINS

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Chemical site-selective modification of proteins is a powerful tool for (**i**) accessing and understanding structure-activity relationships of different post-translational modifications (PTMs), and (**ii**) building homogenous therapeutic proteins such as carbohydrate-based vaccines or antibody-drug conjugates (ADCs). Here, I will present different strategies to install different PTM's and cytotoxic drugs on proteins in a controllable and specific manner.

Reaction engineering at cysteine: From disulfides to thioethers, a range of novel reactions and methods that enable controlled, specific modification of proteins at cysteine were developed. These methods are efficient strategies to access post-translational modifications such as phosphorylation, glycosylation, prenylation, or acetylation and methylation of lysine residues on proteins in a controllable, defined manner.

Traceless, homogenous ADCs for cancer therapy: Using a vascular targeting approach, it was demonstrated for the first time that non-internalizing antibody-drug conjugates (ADCs) may be used to mediate strong anti-tumor activity *in vivo*. Coupling technology was based on direct cysteine modification with potent thiol containing cytotoxic drugs that yielded chemically defined, traceless ADCs. This novel strategy allows **a**) the progressive amplification of drug release, as tumor cell lysis mediates glutathione and cysteine release to the surrounding tissue and **b**) results in a strong anti-tumor activity *in vivo*, as demonstrated in three different syngeneic immunocompetent models of murine cancer that are not cured by conventional cytotoxic agents alone.

Keywords: *Synthetic Biology; Synthetic methods; Protein modifications; Bioorganic chemistry; Drug-delivery;*

Supramolecular Chemistry – II

O-385

UNPRECEDENTED BISTABLE HOST-GUEST COMPLEXES OF CUCURBIT[6]URIL AND AROMATIC DIAMMONIUM SALTS

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Since the first reported cucurbit[6]uril (CB[6]) complex with dihydrochloride salt of *bis*-1,4-(aminomethyl)benzene,[1] CB[6] complexes have been widely used for the construction of pseudorotaxanes and rotaxanes that exhibited interesting dynamic, structural, and functional properties.[2] However, while linear aliphatic diammonium salts readily form stable host–guest complexes of CB[6],[3] the ability of CB[6] to host aromatic compounds has not been investigated.

Recently we have reported that 4-aminobipyridine derivatives form strong 1:1 inclusion complexes with CB[6], whereas the *N,N*-bis(2,2'-bipyridine)xylylenediamine analogue forms a strong 1:2 complex with CB[6] at room temperature[4] and we report here the scoop of host–guest complexes of CB[6] with various 1,4-bis(alkylaminomethyl)benzene guests.[5] Interestingly, these complexes are found to exhibit two stable binding modes with an unexpectedly high barrier between them. The highly stable 2:1 complexation mode that is formed at room temperature, is found to be a kinetic product, and can be converted to the thermodynamic 1:1 complex upon prolonged heating to 100 ºC. The latter is a very stable rotaxane despite the fact that it lacks bulky end groups.

The structural and dynamic properties of the various complexes, the kinetic and thermodynamic binding parameters, as well as different chemical reactivity towards the azide–alkyne [3+2] cycloaddition reaction (click chemistry), will be discussed.

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Keywords: *host-guest systems; click chemistry; rotaxanes;*

Supramolecular Chemistry – III

O-386

SUPRAMOLECULAR SENSORS

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Selectivity is one of the key issues involved in developing new, efficient chemical sensors.[1] The use of supramolecular structures has proven to be one of the best approaches to generate new materials with molecular specificity for chemical sensing. However, the direct translation of the molecular recognition properties of a given receptor from solution studies to the solid devices is not trivial, since nonspecific interactions such as dispersion forces, and material properties, like surface morphology, come into play.[2] In this lecture, I will report our recent efforts to produce specific supramolecular sensors using phosphonate cavitands as receptors. The implementation of the molecular recognition paradigm throughout the whole sensing chain will be highlighted through selected examples from our own work. Particular emphasis will be given to strategies to remove the two bottlenecks hindering the exploitation of synthetic receptors in supramolecular sensing, namely the precise transfer of the intrinsic molecular recognition properties at the gas-solid and liquid-solid interfaces and the high fidelity transduction of the interfacial molecular recognition events.

In this contribution three examples will be illustrated:

- Solid-gas interface: Fluorescent cavitands as selective layers for the specific detection of C_1-C_4 alcohols in the gas phase.[3]
- Solid-liquid interface: Exclusive detection of sarcosine in water and urine with cavitand-functionalized SWCNTs and cavitand-functionalized silicon wafers.[4,5]
- Nanomechanical recognition of *N*-methylated derivatives.[6]

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Keywords: *Cavitands; Interfaces; Sensors;*

Supramolecular Chemistry – III

O-387

AZOBENZENE MACROCYCLIC CHIROPTICAL SWITCHES

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Light-driven molecular machines have attracted intensive attention for their potential applications in the field of optical data processing and storage. One of the alternative strategies for the non-destructive readout is represented by utilization of their chiroptical properties. Photochromic diaryldiazene unit undergoes significant change in molecular geometry upon *trans-cis* isomerization which has been successfully explored for construction of chiroptical switches in combination with binaphthalene moiety as conformation sensitive chiral unit (changing dihedral angle between naphthyl units).

Our results on the synthesis and characterization of macrocyclic switches consisting of photochromic diazene and binaphthalene chiral moiety attached via suitable linkers will be reported. In comparison to the previously reported analogues with more flexible propan-1,3-diyldioxy linkers, the derivatives with more rigid acrylamide and urea linkers exhibit advanced switching performance: switching of CD signal intensity up to 1:3 for compound with acrylamide linker, or even switching the signal sign for compoud with urea linker.

Keywords: *azo compounds; binaphthyl derivatives; chiroptical switches;*

Supramolecular Chemistry – III

O-388

SELF-ASSEMBLED TTF-BASED REDOX-ACTIVE RECEPTORS: FROM 2D POLYGONS TO 3D CAGES

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The methodology of self-assembly driven by metals (typically Pt, Pd) allowed the preparation of a large number of molecular polygons (triangle, square,...) and polyhedrons (cubes, prisms, …) presenting remarkable properties.[1] For instance, the water-soluble cage described below by Fujita *et al* showed surprising catalytic activities.[2]

Nevertheless, very few electro-active polygons or polyhedrons have been described, and none presents an electron-rich cavity. In this context, we have initiated a project to elaborate new self-assembled discrete structures incorporating redox-active walls based on tetrathiafulvalene (TTF).[3]

We recently described the first self-assembled molecular square and triangle integrating TTFs units, reversibly oxidizable and able to complex the electron-poor fullerenes C_{60} or C_{70}.[4]

In this communication, we will focus on our last results in this area, and in particular on several new three dimensional capsules based on TTF, bispyrrolo-TTF (BPTTF) and extended-TTF (exTTF) based-ligands (see below), and on their capability to bind electro-deficient units.

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Keywords: *Sulfur heterocycles; Self-assembly; Supramolecular chemistry; Molecular recognition;*

Supramolecular Chemistry – III

O-389

MODULAR SYNTHESES OF POROUS ORGANIC CAGE COMPOUNDS

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Discrete organic cage compounds are a new family of porous materials besides the well investigated metal organic frameworks or zeolites.[1] They are synthesized from readily available precursors in one-pot by reversible Schiff-base reactions. In contrast to porous networks, cage compounds are soluble in common solvents and thereby, for example porous thin films can be casted.[2] Recently, the reaction of triptycene triamine with different salicyldialdehydes to [4+6] cage compounds was introduced. The amorphous material as well as the crystalline material of the [4+6] cage compounds have a high nitrogen gas uptake at 77 K which results in Brunauer-Emmett-Teller (BET) surface areas up to 2071 m^2 g^{-1}.[3] By a similar approach, using other dialdehydes, various shape persistent cage compounds of different sizes and functionalities in the interior or exterior of the molecules can be rationally constructed.[4, 5] The syntheses and material properties of those cage compounds will be discussed.

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Keywords: *Cage compounds; Crystal engineering; Schiff bases;*

Supramolecular Chemistry – III

O-390

ONE-POT REGIOSELECTIVE SYNTHESIS AND X-RAY CRYSTAL STRUCTURE OF A STABLE [60]FULLERENE TRISADDUCT WITH THE EEDGE,EFACE,TRANS-1 ADDITION PATTERN

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The tether-directed remote functionalization method is a sophisticated and powerful approach which has been applied successfully for the regioselective functionalization of C_{60}. To access three-dimensional fullerene architectures, absolute control of the regioselectivity of tris-additions on the spherical fullerene carbon network is needed, since compared with bis-additions on C_{60} the number of the possible trisadducts is dramatically increasing. As such, the design of appropriate tethers becomes a more demanding task. Among the 46 possible trisadducts of C_{60} (excluding the ones having a *cis*-1 position relationship), we targeted the *e*,*e*,*trans*-1 for the following reasons: **a**) this addition pattern cannot be accessed by stepwise Bingel cyclopropanations on C_{60}, **b**) the *e*,*e*,*trans*-1 trisadduct is a synthetically valuable precursor for the synthesis of mixed [3:3] hexakisadducts with different types of addends located at octahedral sites. By varying the nature or the hydrophobic/hydrophilic character of the different organic addends, globular dendrimers, lipofullerenes and novel functional materials were synthesized and studied, and c) the synthesis of the *e*,*e*,*trans*-1 trisadduct of C_{60} has been reported before but required multiple synthetic steps and chromatographic separations. The Bingel functionalization of C_{60} with a structurally novel tether equipped with three reactive malonate groups afforded a C_{2v}-symmetrical e_{edge},e_{face},*trans*-1 trisadduct in a complete regioselective manner and in the excellent yield of 65 %. The [60]fullerene trisadduct showed pronounced ability to crystallize and gave X-ray quality single crystals for analysis. The synthesized e_{edge},e_{face},*trans*-1 fullerene trisadduct represents a novel and attractive molecular structure due to the three-dimensional cavities that form between the tether and the fullerene skeleton, equipped with oxygen atoms and aromatic rings. Furthermore, the designed tether enhances the crystallizability of fullerene adducts and this might be useful for the functionalization of higher fullerenes where the assignment of the addition patterns is difficult by NMR spectroscopy.

Keywords: *Fullerenes; Macrocycles; Regioselectivity; Template Synthesis; X-ray Diffraction;*

Supramolecular Chemistry – III

O-391

ANION-PI INTERACTIONS AND HALOGEN BONDS IN ACTION

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The creation of supramolecular functional systems is of paramount importance. In this context, the available interactions to create function should be widened as much as possible. Ion transport systems are practically well suited to probe for the functional relevance of otherwise elusive interactions, because only weak contacts are needed for activity, whereas stronger contacts cause inactivation; a similar Goldilock-type situation exists in catalysis.

Whereas most of the synthetic transport systems relay on intrinsically hydrophilic non-bonding interactions, especially hydrogen bonds, the possibility to use hydrophobic analogs appeared very promising. Therefore, the application of less recognized non-covalent interactions to anion transport systems seemed most fitting.

Early work includes transport with anion-π interactions[1], here the focus is on anion transport systems that operate with halogen-bond donors. Their strength, directionality and hydrophobic nature seemed ideal for this purpose.

Exploiting known scaffolds (*i.e.* calixarenes), we have shown that anion transport in bilayer model systems can be achieved with halogen bonds. However, these initial examples required assistance from ion pairing and were too complex[2]. Therefore, we simplified the concept and minimized the system to the extreme. This approach provided access to extremely small molecules, down to highly volatile transporters containing one single carbon only, that are capable to self-assemble in lipid bilayer membranes and form supramolecular anion transport systems.

These systems were studied for anion transport in fluorogenic vesicles as well as in planar bilayer conductance experiments, in the solid state with x-ray crystal structures and modeled *in silico*. The outcome is a surprisingly clean, leakage free, highly selective, non-ohmnic and minimalist transport system.

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Keywords: *Supramolecular chemistry; Noncovalent interactions; Anions;*

Supramolecular Chemistry – III

O-525

PHOSPHONATED SMALL MOLECULES - A MULTITALENT IN FUEL CELL APPLICATIONS -

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State-of-the-art separator materials often consist of sulfonic acid based perfluorinated polymers such as Nafion®. The operation temperature of these materials is limited to the boiling point of water since proton conductivity strongly depends on the hydration of the membrane. Water-based proton-exchange membranes (PEMs) show certain disadvantages such as poor carbon monoxide tolerance and significant water transport through the electrolyte. Therefore, non-water-based PEMs providing high protonconductivity at intermediate temperatures (110 - 150°C) and low humidity are one of the biggest challenges for new separator materials.

On-going research has focused on the development of Nafion®-like materials which present a nanophase separation between a hydrophobic polymer main chain and acidic moieties. Another concept concerns the use of anhydrous protic ionic liquids which do not require humidification for proton transport. However, despite high conductivities a critical issue that still severely hampers the use of these electrolytes in fuel cell applications is their volatility as well as their instability.

A different approach to achieve proton mobility by self-organization of small phosphonated molecules such as hexakis(*p*-phosphonatophenyl)benzene could be recently demonstrated.[1,2]

For the development of novel separator materials based on this concept phosphonic-acid containing molecules with different geometry and substitution patterns were synthesized and characterized. These crystalline materials self-assemble into well-defined superstructures containing a proton-conducting periphery and present high as well as constant proton conductivities in the solid state. By incorporation of electron-conducting moieties into these organic crystals, a mixed proton-electron-conducting material is being envisaged which has only been achieved for inorganic or composite materials up to now.

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Keywords: *Conducting material; Fuel cells; Phosphorylation; Proton transport; Self-assembly;*

Frontiers and Advances of Organic Chemistry – I

O-488

NEW DIRECTIONS IN ORGANOCATALYSIS

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The lecture will present new activation modes in organocatalysis which allow for the development of new reaction concepts

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Frontiers and Advances of Organic Chemistry – I

O-489

MICRO FLOW CHEMISTRY – NEW POSSIBILITIES FOR SYNTHETIC CHEMISTS

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Until recently, many reactions have been exclusively performed in batch processes. With the advent of microfluidics, significant effort has been devoted to develop a wide variety of continuous-flow techniques to facilitate organic synthesis.[1, 2] Microreactor technology offers several advantages compared to traditional batch reactors, such as, enhanced heat- and mass-transfer and the possibility to integrate several reaction steps and subsequent separations in a single streamlined process.

In this presentation, we will give an overview of some interesting aspects of flow chemistry within the realm of so-called *Novel Process Windows*.[3] This involves microflow results obtained in:

- Buchwald-Hartwig Aminations: this section details on handling of solid forming reactions in microfluidic systems;[3a, 3e]
- Suzuki-Miyaura Cross-Coupling Reactons: the feasibility to perform multistep reactions in microflow will be described in this part;[3b, 3d]
- Pd-catalyzed Fluorinations: our efforts towards the development of an accelerated fluorination process in flow will be discussed in this fragment;[3c]
- Click chemistry: we will conclude with a discussion of our efforts to develop a continuous copper scavenger unit.[3f]

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Keywords: *Microreactors; Amination; fluorine; Click chemistry; Cross-coupling;*

Frontiers and Advances of Organic Chemistry – I

O-490

NITROAROMATIC EXPLOSIVES SENSING USING NON POROUS, NANO-ORGANIZED FLUORESCENT OLIGOPHENYLENEETHYNYLENE FILMS: HOW DOES IT WORK?

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The use of explosives in terrorist attacks has created a strong demand for explosives vapor sensors that would be suitable for suspicious luggage checking and forensic analysis. Fluorescence quenching of phenyleneethynylene compounds by nitroaromatic explosives is now a well-established method for sensing purposes.

A great deal of attention has been focusing on the design of polymer structures incorporating sufficient porosity to allow diffusion of the nitroaromatic molecules in the film. However, some efficient non polymeric phenyleneethynylene derivatives have been reported. For these compounds, a rationale explaining their ability to detect nitroaromatic vapors is clearly lacking.

The crystal structures of films of two similar phenyleneethynylene compounds displaying different behaviors were investigated. The first, Di8, bearing diimine moieties, is very sensitive to nitroaromatics but the second, unsubstituted compound shows poor responses. First it was shown that both non-porous films exhibited a high degree of crystallization and a preferred orientation, and that the crystal structure was identical in films or single crystals. Analysis of the very specific molecular arrangement within the crystals revealed that the fluorescent conjugated pi-structure of the non-responsive compound is highly tilted from the surface so that it can hardly be accessed by nitroaromatic vapors. On the contrary, the pi-structure of the efficient compound Di8 is readily available since it is almost parallel to the surface. This arrangement was also observed in films of another related product that also exhibited excellent sensing performances, thus consolidating the hypothesis.

Moreover, exciton migration within the films of Di8 was clearly observed through time-resolved fluorescence experiments. This explains how most of the fluorescence of these non-porous films can be quenched even at very low concentrations of nitroaromatic species.

Therefore, for the first time, structural data are provided on organic thin films to better understand the structure/sensing ability relationships for non porous phenyleneetynylene compounds.

Keywords: *sensors; fluorescence; thin films; nanostructures; supramolecular chemistry;*

Frontiers and Advances of Organic Chemistry – I

O-491

REDOX-NEUTRAL BIO-CASCADE TO AMINES FROM PRIM-ALCOHOLS

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While to transform primary alcohols to amines has been vividly investigated for metal catalysts applying the so called "borrowing hydrogen" methodology,[1–3] no such process has been reported for primary alcohols employing biocatalytic methods.

A biocatalytic cascade was thus designed: In the first step an alcohol dehydrogenase (ADH)[4, 5] catalyzed the oxidation of the alcohol consuming NAD^+ leading to the formation of the aldehyde and NADH.

In the second sequential simultaneous step, an ω-transaminase (ω-TA) is doing the amination reaction transferring the amine group from L-alanine to the aldehyde creating pyruvate, which is recycled by an NADH-dependent alanine dehydrogenase (AlaDH) using an ammonium salt as the nitrogen source regenerating the cofactor as well as the amine donor.

Acknowledgement: *The research leading to these results has received funding from the European Union's Seventh Framework Programme FP7/2007-2013 under grant agreement no 245144 (AmBioCas) and Evonik.*

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Keywords: *amination; primary alcohols; biocatalysis; Nylon; cascade reaction;*

Frontiers and Advances of Organic Chemistry – II

O-492

ARTIFICIAL PHOTOSYNTHESIS – LOW DIMENSIONAL CARBONS

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Carbon is the key to many technological applications that have become indispensable in our daily life. Altering the periodic binding motifs in networks of sp^3-, sp^2-, and sp-hybridized C-atoms is the conceptual starting point for a wide palette of carbon allotropes. To this end, the past two decades have served as a test-bed for measuring the physico-chemical properties of low-dimensional carbon with the advent of fullerenes (0D), followed in chronological order by carbon nanotubes (1D), carbon nanohorns, and, most recently, by graphene (2D). These species are now poised for use in wide-ranging applications.

Expanding global needs for energy have led to a significant effort to develop alternatives to fossil fuels. While alternative sources for energy are already in use, they comprise a small percentage of the energy demands needed to carry us through the 21st century. No single source will solve the global needs, but the development of photovoltaics has vast potential as a point-of-use power source. Recent work has shown that hybrid photoelectrochemical efforts with a percolation network of photon absorbers coupled to anelectron/hole transporter in combination with advanced photon management are the ideal design for realizing breakthroughs in high photon conversion efficiencies suitable for the catalysis of water.

I will report on our efforts regarding a unifying strategy to use the unprecedented charge transfer chemistry of 0D fullerenes, the ballistic conductance of 1D carbon nanotubes, the semiconducting features of carbon nanohorns, and the high mobility of charge carriers in 2D graphene, together in a groundbreaking approach to solving a far-reaching challenge, that is, the efficient use of the abundant light energy around us.

Keywords: *Carbon Allotropes; Solar Energy Conversion;*

Frontiers and Advances of Organic Chemistry – II

O-493

ACTIVATION OF EPOXIDE BY PHENOLIC OXIDATION, A NEW ENTRANCE IN CASCADE REACTION

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Phenol is ubiquitous in nature and is a common starting material for the building of various and complex secondary metabolites. Over the past few years, we have been involved in the study of cascade reactions triggered by phenolic oxidation.[1] By oxidizing phenol with hypervalent iodine reagent, we demonstrated that an intramolecular ketone can be trapped by the corresponding phenoxenium species resulting in the activation of subsequent reactive species in cascade manner.[2]

In this communication, we wish to report our last endeavours by the transposition of this activation process from ketone to epoxide groups. The resulting species turns out to be highly efficient to initiate new cascade sequences giving rise to complex structures. We will also present examples of enantioselective cascade reactions involving enantioselective epoxidation and phenolic oxidation.

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Keywords: *Domino reaction; Epoxidation; Hypervalent compound; oxidation; Spiro compound;*

Frontiers and Advances of Organic Chemistry – II

O-494

BUILDING PRIVILEGED COMPLEXITY WITH CASCADE TRANSFORMATIONS: FROM RING- TO FUNCTIONAL DIVERSITY

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Compound collections designed on the basis core scaffolds of of natural products or the privileged motifs are expected to be enriched in biochemical and biological activity. This calls for developing efficient chemical transformations wherein further molecular complexity (ring-structures and sp3 character) and diversity (functional groups and carbo- and heterocyclic rings) can be generated around these core-structures and which should be amenable to compound collection format.[1] Cascade or domino reaction sequences can rapidly built up molecular complexity and thus could prove highly useful in synthesis of focused compound libraries based on natural products core structures.[2] We have successfully developed new cascade reaction sequences leading to compound collections around benzopyrone, indoloisoquinoline and indoloquinolizine core structures of natural products. This presentation will summarize the implementation of different modes of catalysis *i.e.* organo-, nucleophilic and Bronsted acid and coinage metal catalysis to facilitate diverse cascade reactions that transform the easily available substrates into the desired complex natural product inspired compounds. A glimpse into how such molecules help understand complex biological phenomenon[3] and how the ring-diversity translates into functional-diversity shall also be presented.

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Keywords: *Alkaloids; Annulation; Domino reactions; Molecular diversity; Natural products;*

Frontiers and Advances of Organic Chemistry – III

O-495

SYNTHETIC SUPRAMOLECULAR SYSTEMS AT WORK

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This lecture will summarize recent progress with design, synthesis and evaluation of functional supramolecular systems. The unifying theme is transport, topics of interest include the transport of electrons and holes in photosystems, the transport of anions and cations across lipid bilayers, and the transport of larger molecules for sensing applications and cellular uptake.

To create oriented photosystems, we will have to learn how to build with high precision directly on surfaces. To contribute new solutions for this old problem, zipper assembly has been introduced first. Combining LBL with stick-end technology, zipper assembly has afforded double-channel architectures with oriented antiparallel redox gradients. Looking for more user-friendly alternatives, self-organizing surface-initiated polymerization (SOSIP) has been developed next. This method uses ring-opening disulfide exchange polymerization from templating initiators on the surface. Hard to get but easy to use, SOSIP is now being applied to topics such as templated self-sorting for the transcription of 2D information into 3D architectures. Moreover, stack exchange has been introduced to drill big holes into SOSIP architectures and build multi-channel systems with multicomponent gradients, ultimately composed of naphthalenediimides, perylenediimides, squaraines, phthalocyanines, porphyrins and fullerenes.

As far as the transport of ions in lipid bilayers is concerned, current interest focuses on the expansion our repertoire of established interactions we have in hand to create function. Examples include anion-macrodiple interactions, anion-π interactions, and halogen bonds. To proof the functional relevance of these less common interactions beyond any doubt, the size of the transporters had to be reduced to an absolute minimum. Driven to the extreme, this reductionism resulted in the first example of clean, leakage-free, cooperative, highly voltage-dependent and highly anion selective transport with the smallest possible organic transporter, a molecule with one single carbon only, and a boiling point of -22 ºC.

Keywords: *photosystems; ion transport; surface-initiated polymerization; templated self-sorting; halogen bonds;*

Frontiers and Advances of Organic Chemistry – III

O-496

PRECIOUS METAL DOPED ZEOLITES IN ENVIRONMENTAL CATALYSIS

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Precious metal exchanged zeolites can be used for various environmental applications allowing the reduction off necessary precious metal doping in comparison to conventional combustion catalysts. A typical example is the use of Pt and Pd exchanged zeolites for stationary VOC combustion. The main feature of zeolite based catalysts is the possibility to incorporate the precious metals into the pores and cavities of the zeolite framework. This will hinder the precious metal clusters to grow up resulting in a decreased catalytic activity.

However, the capability of the zeolite cavities to take up precious metal species is limited. The excess of precious metals which are then deposited on the outer crystallite surface can undergo rapid sintering during exposure of the catalyst to elevated temperatures. For effective incorporation of precious metals into zeolites, the kind of precursor applied and calcination conditions are of significant relevance. To discriminate between "internal" and "external" precious metal clusters, infrared spectroscopy with application of sensor molecules and selective poisoning techniques can be applied.

Frontiers and Advances of Organic Chemistry – III

O-497

DOPED PI-CONJUGATED ORGANIC EMITTERS: SYNTHESIS, PROPERTIES AND SUPRAMOLECULAR ORGANIZATION

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The development of organic-based polymers and of their hybrid derivatives paves the way towards materials with a continuously tunable energy gap from the IR to the deep UV. Specifically, there is a growing demand for light-emitting devices (LEDs) in the deep UV region, for a variety of applications where high photon energy is necessary for either processing or sensing/characterisation purposes (UV lamps for photodynamic therapy, water sterilization systems, "solar-blind" photodetectors, to name a few). A possible engineering strategy meeting these requirements would be to tune the electronic properties of the material by combining molecules with a similar carbon-based structures replacing every pair of carbon atoms rings by boron and nitrogen atoms. In this respect, borazine rings (Stock in 1926) are good candidates. However, the sensitivity toward water has hampered their exploitation in current technologies. In this report, we will describe the synthetic efforts toward the synthesis of water-stable borazine derivatives. Fluorescence studies in solution and at the solid state showed the presence of a strong UV-emission band in the UV region. The synthesis of unprecedent unsymmetrical borazine derivatives and borazene linear modules will be shown as well as their organization on surfaces. Novel H-bonding interactions involving boronic acids will be also discussed showing their potentials as alternative molecular synthones in molecular recognitions.

Keywords: *Boron; Hydrogen bonds; Donor acceptor systems; Self-assembly; Supramolecular Chemistry;*

Frontiers and Advances of Organic Chemistry – III

O-498

HIGHLY DISPERSED PALLADIUM NANOPARTICLES ON MESOCELLULAR FOAM: AN EFFICIENT AND RECYCLABLE HETEROGENEOUS CATALYST FOR ALCOHOL OXIDATION

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Oxidation reactions are of fundamental importance in nature, and they are key transformations in organic synthesis. During the past decades, a large number of oxidation methods have been developed. Despite the development, traditional oxidation methods employing stoichiometric amounts of high-valent metal reagents are still commonly used in the production of a large number of organic compounds. These oxidations lead to large amounts of toxic metal waste and therefore it exists a considerable need for the development of new and more efficient catalytic oxidation methods in industrial chemistry. To meet the needs of high efficiency and "green chemistry", processes that employ transition metals as substrate-selective catalysts and use environmentally friendly and cheap oxidants, such as molecular oxygen, have consequently emerged as a topic of major research. In these oxidations the substrate is oxidized and molecular oxygen is converted to water. The catalyst is essential since direct oxidation of organic substrates by molecular oxygen is associated with high energy barriers of electron transfer.

We have recently developed a heterogenous catalyst consisting of palladium nanoparticles immobilized on siliceous mesocellular foam and it has been shown to be able to efficiently catalyze the oxidation of a wide scope of primary and secondary alcohols, using molecular oxygen as terminal oxidant. Furthermore, the catalyst displayed excellent recyclability and negligible leaching, which are two important factors to consider when applying a catalyst in industrial and pharmaceutical applications.

Keywords: *Oxidation; Heterogeneous Catalysis; Green Chemistry; Alcohols; Nanoparticles;*

Frontiers and Advances of Organic Chemistry – III

O-499

METAL-CATALYZED CASCADE REACTIONS OF ALKYNES: USEFUL PROTOCOLS FOR SYNTHESIS OF POLYCYCLIC AROMATIC HYDROCARBONS AND OLIGOENES

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Metal-catalyzed reactions for carbon-carbon bond formation are the focus of extensive research in organic synthesis. These reactions are useful tools for constructing a variety of valuable and important products. Unsaturated substrates, such as alkenes, alkynes, and others, are suitable for use in these reactions because they easily form π-complexes, and subsequently undergo migratory insertion from their coordination sphere. This phenomenon makes the reaction very efficient, even under mild conditions. Recently, my coworkers and I have successfully developed several synthetic methods for preparing numerous polycyclic aromatic hydrocarbons and oligoenens, including 8,8a-dihydro-cyclopenta[*a*]indenes,[1] cyclopenta[*def*]phenanthrenes,[2] zethrenes,[3] pyrroloarenes,[4] benzo[*k*]fluoranthene-based linear acenes,[5] phenanthroindolizidine alkaloids,[6] highly curved buckybowls[7] and octatetraenes.[8] Most of these compounds exhibit interesting physical properties, and can be applied to organic materials. For example, benzo[*k*]fluoranthene-based linear acenes display strong blue photoluminescence, and are used for efficient deep blue organic light-emitting devices.[9] In addition, phenanthroindolizidine alkaloids have strong antitumor effects.

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Keywords: *Alkyne; Palladium; Polycyclic Aromatic Hydrocarbon; Oligoene;*

Novel Materials – I

O-096

PI-SIGMA* STATES IN THE PHOTOCHEMISTRY OF HETEROAROMATIC MOLECULES

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Imidazoles, pyrroles and phenols are key components of the long wavelength chromophores in nucleobases and aromatic amino-acids like histidine, tryptophan and tyrosine, which dominate the UV absorption spectra of many biological molecules. π^*-π transitions are responsible for these strong UV absorptions, but such heteroaromatic molecules also possess excited states formed via σ^*-π electron promotions. The latter excitations have much smaller absorption cross-sections, and have only recently started to attract much detailed attention. High resolution photofragment translational spectroscopy methods and complementary *ab initio* theory have been used to study H atom loss processes following UV photo-excitation of a progressively more complex range of such heteroaromatics in the gas phase.[1] These studies:

- **(i)** demonstrate that heteroatom–H bond fission following direct excitation to the $1^1\pi\sigma^*$ state or, in phenols, by tunneling under the conical intersection between the $1^1\pi\pi^*$ and $1^1\pi\sigma^*$ potential energy surfaces, can be an important non-radiative decay process in such molecules,
- **(ii)** show that the radical co-fragments are formed in a very limited sub-set of the vibrational states that are accessible, energetically. Identification of these product states provides detailed insights into the non-adiabatic couplings that enable the evolution from parent molecule to eventual fragments, and
- **(iii)** open the way to studies of analogous fragmentation processes in solution – in collaboration with the group of Professor Steve Bradforth at the University of Southern California.[2]

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Novel Materials – I

O-097

CONFORMATIONAL EFFECTS IN SUGAR IONS: SPECTROSCOPIC INVESTIGATIONS OF THE PROTONATED ALPHA AND BETA ANOMERS OF D-XYLOPYRANOSYL IMIDAZOLIUM IN THE GAS PHASE AND IN SOLUTION

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We present direct investigations of the conformational preferences of sugars with a positively charged substituent at their anomeric centre, C-1, which display in solution, a preference for an equatorial conformation - an apparent reversal of the normal anomeric effect. The investigations focus on the protonated monosaccharide, D-xylopyranosyl imidazolium in its α and β forms, first probed in a range of different solvents through NMR measurements and then in the gas phase, i.e. free of solvent or counterion interactions which may have clouded or even overwhelmed the normal anomeric effect. The sugar ions in the gas phase were generated at a temperature ~300-350 K and were subsequently probed through mass selected infrared multiphoton dissociation spectroscopy. The results, when compared and discussed in the light of density functional theory, ab initio and natural bond orbital calculations, expose the possible origins of the reversed conformational preference and provide a better understanding of the factors controlling conformational choice.

Keywords: *conformational effects; sugars; spectroscopy; gas phase; biomolecules;*

Novel Materials – I

O-098

CATALYTIC STUDIES OF FeS_2 TOWARDS AMMONIA SYNTHESIS UNDER AMBIENT CONDITIONS

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The synthesis of ammonia over an iron catalyst, via the Haber-Bosch process, is one of the most important large-scale industrial reactions underlying the modern global economy. Essential for the manufacture of artificial fertilisers, this single process is reckoned to be responsible for feeding up to one sixth of the world population. On the other hand, such high temperatures and pressures are necessary to achieve economic performance that the Haber-Bosch process alone is thought to consume up to one percent of all man-made energy production.[1] At this scale, even a marginal improvement in efficiency would imply enormous environmental benefits, not to mention inevitable economic rewards. Of all the industrial processes, ammonia synthesis is arguably the instance for which tuning catalytic efficiency is most urgently required.

In nature, by way of contrast to the Haber-Bosch process, the enzyme nitrogenase achieves much the same end under ambient conditions. Efforts of protein crystallography have gradually unveiled that the active sites of nitrogenase are composed of three distinct FeS_x nanoclusters which cooperatively accomplish the electron transfer and the N_2 reduction processes.[2, 3]

In the light of the above understanding, we are investigating NH_3-related reactions on Iron sulfide surfaces. In the presentation, we will discuss the surface chemistry of N_2, H_2 and NH_3 on a pyrite single crystal surface. The gas-surface interactions are investigated by a combination of spatially averaging and localized surface science techniques to ascertain whether NH_3 synthesis is favourable iron sulphide, with a view to establishing their corresponding reaction mechanisms.

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Keywords: *Ammonia synthesis; Iron sulphide; Surface science;*

Novel Materials – I

O-099

UV PHOTODISSOCIATION DYNAMICS OF THIOANISOLES: THE EFFECT OF SUBSTITUTION

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In this work, both experimental and theoretical, results from the UV photodissociation of thioanisole[1] in the gas phase are reported. The effect of substitution on the dynamics of the photodissociation has also been studied, by introducing a methyl (CH_3) group, as a substituent, in para- position. The dissociation has been studied using Velocity Map Imaging (VMI) technique and detecting the produced, after the S-CH_3 bond fission, methyl fragments in their ground vibrational state (v=0). Both velocity and angular information are presented. The experimental results are accompanied by high accuracy ab initio calculations, which give the shape of the Potential Energy Cuts (PECs) of the ground and the first two excited electronic states, along the S-CH_3 coordinate. Such gas phase studies are an essential precursor to on-going ultrafast pump-probe investigations of the photochemistry of these molecules in solution.

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Keywords: *Photochemistry; Ab initio calculations; Substituent effects; UV/Vis spectroscopy; Laser spectroscopy;*

Novel Materials – II

O-100

THE HYBRID LANGMUIR-SCHAEFER DEPOSITION – A NEW BOTTOM-UP APPROACH TO CREATE LOW DIMENSIONAL FUNCTIONAL NANOSTRUCTURES

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In recent years, low-dimensional assemblies have assumed remarkable importance due to their outstanding physical, chemical and biological properties which make them attractive for photophysical and electrical applications as well as for catalysis, molecular separation, drug delivery and biosensing. Controlling both the organization of the assemblies and their properties through simple external parameters led to the creation of new tailored functional materials.

An easy method to produce such materials with excellent of control combines self-assembly and Langmuir-Blodgett assembly. I shall demonstrate how this method allows the assembly of hybrid materials based on the fact that graphene oxide or clay nanosheets act as 2D template for reaction or grafting of a variety of guest species (in our case: C_{60}, Ni_8 molecular magnets, Prussian Blue analogues, metal nanoparticles). Prefect layer-by-layer growth and control at the molecular level allow one create entirely novel architectures whose final structure is encoded in the shape and properties of the clusters or molecules that are used. Interesting new properties emerge: for example 2D or 0D Prussian Blue analogue structures can be formed, which differently from 3D crystals, show new superparamagnetic-spin glass properties with high blocking glass temperature. The versatility of the approach will be illustrated also in the case of grapheme oxide – metal nanoparticle assemblies where one can choose to either synthesize the nanoparticles in situ or graft already formed nanoparticles on the sheets obtaining materials with different magnetic properties.

Keywords: *Self-assembly; Clays; Graphene; Langmuir-Blodgett films; Materials Science;*

Novel Materials – II

O-101

THEORETICAL SEARCH FOR ENVIRONMENTALLY FRIENDLY FIRE EXTINGUISHING SUBSTANCES

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Since the advent of the Montreal Protocol in the 1990, which banned the manufacture of a variety of halogenated compounds including the fire suppressant CF_3Br (because of ozone depletion action), there has been a strong interest in development of new chemically active fire suppressants. One of the classes of compounds, that are under consideration are phosphorus-based agents, such as DMMP (dimethyl methylphosphonate), TMP (trimethylphosphate) and others. Extinction measurements on non-premixed, atmospheric-pressure flames have demonstrated DMMP to be a highly effective suppressant (2-4 times more effective than CF_3Br).[1] The mechanism for phosphorus-based inhibition is believed to be catalytic recombination of flame radicals ($H^{?}$, $O^{??}$, $OH^{?}$) by phosphorus-containing radicals[2, 3] formed following the decomposition of parent compounds.[2, 4] The influence of phosphorus-containing compounds (PCCs) on radical concentrations in flames has been demonstrated experimentally, but there are still some not properly understood details of inhibition mechanisms. The ab initio quantum-chemical calculations in the 6-31G** basis set of the destruction ways of phosphorus-containing fire suppressant compounds as well as the interaction energy of destruction products with flame radicals have been provided to investigate the inhibition mechanisms. It was shown, that the inhibition action could be done by molecules of DMMP and TMP but much more extend by the destruction products: $HOPO_2$, HOPO, PO_2 and PO. This results are in good agreement with experimental papers.[3, 4]

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Keywords: *quntum-chemical calculation; flame radicals; fire extinguishing substances;*

Novel Materials – II

O-102

INFLUENCE OF SUPPORT CONFINEMENT ON IONIC LIQUID CRYSTAL BASED CATALYSTS

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Thermodynamic and physical properties of liquid crystalline systems are modified by confinement in volumes of mesoscopic dimensions. Ionic Liquids (ILs) are molten salts with melting point below 100 °C. They have a liquid crystalline behaviour (ILC) when containing long alkyl chains. We aim at understanding the influence of confinement on transition metal catalysts dissolved in ILCs into porous supports, for the resulting ordered mesophase should lead to increased catalytic selectivity. These IL-based systems are called “Supported Ionic Liquid Phase” (SILP) catalysts. In a first step, different loadings of the ILCs 1-octadecyl- and 1-hexadecyl-3-methylimidazolium trifluorosulfate $[C_{18}C_1Im][OTf]$ and $[C_{16}C_1Im][OTf]$ confined in increasing support pore sizes are studied using Differential Scanning Calorimetry (DSC) and Diffuse Reflectance IR Fourier Transform Spectroscopy (DRIFTS). The results reveal an influence of the confinement on the smectic-to-liquid phase transition and the existence of a contact layer in the order of 2 nm thickness. The latter shows a single glass transition at temperatures 30 K lower than that of the bulk.[1] In a second step, Ni-based and Rh-based complexes are dissolved in the ILC 1,3-didodecylimidazolium tetrafluoroborate $[C_{12}C_{12}Im][BF_4]$, and in $[C_{18}C_1Im][OTf]$ respectively. Investigations on these systems using IR Reflection Absorption Spectroscopy (IRAS) on extended surfaces and DRIFTS on powders show retained liquid crystalline transitions for a ratio from 1 to 10 wt%.[2] This behaviour remains while measuring operando during the hydroformylation of olefins, thus permitting to measure the influence of the phase transition on the catalytic selectivity.

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Keywords: *confinement; infrared; operando; ionic liquid; transition metal;*

Biointerface and Colloids

O-103

INORGANIC ROUTES TO SELF-ASSEMBLED COMPLEX SHAPES

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The morphology of crystals is controlled by their growth environment and crystal structure. But above all, structural control restricts the symmetry of any crystal shape to one of the 32 point-symmetry groups (35 when quasicrystals are considered). Crystal structure also imposes discrete angles between faces and discards the possibility of continuous curvature. To break this constriction, life has developed several strategies to built crystalline complex morphologies with continuous curvature but hierarchical textural organization. The formation of such architectures is usually directed by organic molecules or matrices and it is thought they are privative of life and distinguish biogenic shapes from their inanimate, mostly euhedral counterparts. I will review in this communication the existence of chemical routes to complex shapes with continuous curvature made of purely inorganic materials. One of them, called silica biomorphs, are simply made by precipitation of alkaline-earth carbonates in silica-rich media. Thus, aggregates of highly oriented carbonate nanocrystals can be obtained, which display striking non-crystallographic morphologies that mimic primitive life forms.[1] These precipitates are made of millions of nanocrystals that self-assemble expanding the symmetry of the crystalline phase 2/m 2/m 2/m forming first fractal aggregates, then two-dimensional lamellae and finally three-dimensional morphologies with non-crystallographic symmetry. I will present the details of the morphogenesis of these materials at a phenomenological level[2, 3] and will propose a plausible physico-chemical explication based on coupling of silica-carbonate precipitation. Finally, I will comment the advances in the formation of silica gardens,[4] a second type of inorganic route to materials with complex shapes.

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Keywords: *Self-assembly; Nanoparticles; crystal growth; Biomimetic synthesis; Bioinorganic chemistry;*

Biointerface and Colloids

O-104

HOMOTAURINE NITROSATION: A KINETIC STUDY

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Homotaurine (3-aminopropanesulfonic acid) is a taurine analogue present in red alga (Ito, K et al. *Hiroshima Daigaku Suichikusangakubu Kiyo* **1977**, *16*, 77). In spite of being rejected in the treatment of Alzheimer's disease, in some countries it is actually a nutraceutical used as a memory protector (Swanoski, M. T. *Am. J. Health Syst. Pharm.* **2009**, *66*, 1950). Due to its similarity to taurine, homotaurine is expected to react with nitrite (widely present in meat as an antibotulinic agent) in the conditions of the stomach lumen.

The nitrosation of taurine affords an unstable sultone as an intermediate product (Arenas-Valganón, J. et al. *Food Chem.* **2012,** *134*, 986) and since some sultones are "possibly carcinogens for human" (IARC, *IARC monograph 71* **1999**), the study of the nitrosation of homotaurine is of interest.

The nitrosation reaction of homotaurine was studied by measuring the variation in absorbance of the nitrosation mixtures at $\lambda = 371$ nm. Nitrosation mixtures were made by the addition of 0.1 ml of nitrite solution to 3 ml of an acidic solution of homotaurine contained in a cuvette. The initial rate method was used.

The experimental rate equation observed for nitrosation of taurine was:

The order with respect to the initial concentrations of reagents was studied, as well as the influence of temperature and ionic strength on k_{obs}. A strong dependence on pH was observed, a maximum value for k_{obs} being observed at pH ≈ 3.3.

The results have led us to propose a mechanism of nitrosation by N_2O_3 in which the reaction is controlled by a diffusion process, as in taurine nitrosation.

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Keywords: *homotaurine; nitrite; nirosation; kinetics;*

Biointerface and Colloids

O-105

DETECTION OF CHAIN BACKFOLDING IN SIMULATION OF DNA IN NANOFLUIDIC CHANNELS

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With recent nanotechnology advances single DNA molecules can be manipulated and analyzed in new ways. Stretching of double-stranded (ds)DNA in nanofabricated channels has emerged as an innovative technique for the fragment length analysis and genome mapping. Molecular simulations combined with the theories of polymer confinement expand our understanding of single molecule experiments. Since the channel dimensions used in measurements (~ 100 nm) much exceed the DNA chain diameter, the confined DNA chains involve various folds of chain on itself, loops and knots.

In series of papers we have earlier employed Monte Carlo simulations based on a discrete worm-like chain model to compute the chain extension R of DNA as a function of channel dimension. (e.g. *J. Phys. Chem. B*, 2009,113,1843). In this report simulations are used to estimate the amount of backfolding in DNA confined in nanochannels. Since folded structures are much shorter than the straight forms, they tend to significantly reduce the equilibrium extension R. The individual folding-unfolding events can be identified in MC traces.

Simulations revealed that the amount of folded structures (hairpins) in channel-confined DNA molecules can be considerable. At the DNA ends an extensive folding (mainly as the J-type hairpins) is detected in narrow and moderate channel widths representing progressively the Odijk, transition and blob regimes from the polymer confinement theories. In contrast, in DNA internal segments the folding into the Z-type hairpins is substantial only at moderate channel widths in the blob regime; such a folding is limited in the transition region and practically absent in narrow channels in the Odijk regime. The importance of accounting for the local folding in interpretation of the DNA experiments in nanochannels is pointed out.

Keywords: *Computational chemistry; DNA; Molecular modeling;*

Biointerface and Colloids

O-106

NEW KINETIC STUDIES OF THE NITROSATION OF COMPLEX MOLECULES

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The report by Magee and Barnes (Magee, P. N.; Barnes, J. M. *Br. J. Cancer*. **1956**, *10*, 114) that dimethylnitrosamine induces liver cancer when fed to rats prompted the study of the Chemistry and Biology of nitroso compounds. Since then, biologists have mainly been interested in the use of these compounds as models for producing a broad range of cancers, whereas chemists are more interested first in the mechanisms of formation of nitroso compounds and then in blocking or inhibiting the mechanisms of these species (Lijinsky, W. (*Chemistry and Biology of N-nitroso compounds,* Cambridge Univ. Press., Cambridge, 1992).

While *N*-nitrosation reactions are well known, the mechanism for generating *C*-and *O*-nitroso compounds are subject to discussion, especially when a molecule has several competing potentially nitrosatable groups (Williams, D. L. H., *Nitrosation reactions and the chemistry of nitric oxide*, Elsevier, Amsterdam, 2004; González Jiménez, M. et al., *Org. Biomol. Chem.* **2011**, *9,* 7680).

In this work, the nitrosation mechanisms of ethylbenzene, 2-phenethylamine and tyramine (2-(4-hydroxyphenyl)ethylamine) in perchloric aqueous solutions of sodium nitrite were investigated. The mechanisms for the reactions of *N*-nitrosation and aromatic *C*-nitrosation are proposed and discussed. The activation of the aromatic ring and the basicity of the substrate proved to be crucial factors in the rate of the *C*-nitrosation reaction, which was sometimes faster than that of *N*-nitrosation.

Nitrosation reactions were followed kinetically by UV-visible spectrography, measuring the absorbance of the reaction products with a spectrophotometer equipped with a thermoelectric six-cell holder temperature-control system (± 0.1 ºC).

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Keywords: *kinetics; nitrosation; catecholamines; tyramine;*

Biointerface and Colloids

O-107

LOW-TEMPERATURE, SOLID-STATE NMR OF THE V49A BACTERIORHODOPSIN MUTANT

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Bacteriorhodopsin is a proton pump which activates when absorption of a photon causes isomerization of the all-trans retinal ligand present in the protein's binding pocket. The V49A mutant changes the retinal binding pocket, resulting in alterations in the retinal isomer composition and in the kinetics of the protein's photoactivation mechanism. It has also been suggested that the V49A mutation disrupts the interaction between the retinal-K216 protonated Schiff base and its counterion, D85. For these reasons, we chose to investigate the retinal environment in the V49A mutant using solid-state NMR. After acquiring 1D and 2D ^{13}C spectra of the dark-adapted bacteriorhodopsin mutant possessing a retinal ligand labeled at positions C8-C15, C19 and C20, we were able to assign many of the peaks due to labeled carbons. We found that both all-*trans* and 13-*cis* retinal isomers are present and that some of the labeled carbons chemical shifts differ from those previously seen in wild-type bacteriorhodopsin. Our results thus far indicate that the environments of certain carbons along the retinal chain in the V49A bacteriorhodopsin mutant are significantly different from those in wild-type bacteriorhodopsin. Experiments are currently underway to resolve the identities and chemical shifts of overlapping peaks. This data should provide insight into the interaction of the protonated Schiff base and the D85 counterion in the V49A mutant and also the changes in the retinal isomer composition. In addition, the sensitivities of our 1D and 2D spectra are such that we are now able to investigate other bacteriorhodopsin mutants' retinal environments.

Keywords: *NMR spectroscopy; Schiff bases; Chromophores; Membrane proteins;*

Theoretical Chemisry – I

O-232

RECENT EXAMPLES ON RELATIVISTIC EFFECTS IN CHEMISTRY

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Relativistic effects often explain the special properties of

6th-Period elements (Cs-Rn), as compared to their 5th-Period analogues (Rb-Xe). It was recently shown using solid-state calculations that about 80% of the voltage of the lead-acid battery come from relativistic effects.[1] Cars start due to relativity. For the mercury battery, the corresponding contribution is about 30 %.[2] The form of the periodic table up to Z=172 was recently reconsidered using average-of-configuration Dirac-Fock calculations on atoms and ions.[3] The last valence electron left upon ionisation was used to classify the chemical group to which the element should be assigned. Two recent reviews have been compiled, one on the fundamental, mainly QED aspects[4] and another on chemical properties, influenced by relativity.[5] As discussed there, more information is now available on spin-orbit (SO) effects in structural chemistry. The relativistic origin of the yellow colour of gold is now confirmed. The use of quantum chemistry to predict new, simple inorganic species was also reviewed.[6]

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Keywords: *Relativistic effects; heavy-element chemistry; Gold; lead; quantum chemistry;*

Theoretical Chemisry – I

O-233

WHY ARE THE INTERACTION ENERGIES OF CHARGE-TRANSFER COMPLEXES CHALLENGING FOR DFT?

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The description of charge transfer complexes by standard density functionals is highly challenging.[1] Illustrative examples include large overestimation of charge transfer by local and semi-local functionals and inaccurate binding energies in the ground state. We demonstrate that standard density functionals fail to accurately describe interaction energies of charge-transfer complexes not only because of the missing long-range exchange as generally assumed[2] but mostly because of the neglected ubiquitous dispersion interactions.[3] Accounting for the missing dispersion interactions is thus of key importance. These assertions are based on the evaluation of the extent of stabilization due to dispersion using both DFT coupled with our recent density-dependent dispersion correction (dDsC)[4] and high-level *ab initio* computations and reflects the imperfect error-cancellation between the overestimation of charge-transfer and the missing long-range interactions. An in-depth energy decomposition analysis of an illustrative series of 4 small ambidentate molecules (HCN, HNC, HF and ClF) bound together with NF_3 provides the main conclusions which are validated on a typical organic charge-transfer complex (i.e., tetrathiafulvalene-tetracyanoquinodimethane). Only well-balanced functionals such as PBE0-dDsC, LC-BOP-LRD and M06-2X can overcome the difficulties of standard density functionals for charge transfer complexes. These results parallel the benchmarking on 341 diverse reaction energies where these functionals were among the best hybrid density functionals.[4]

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Keywords: *Density functional theory; noncovalent interactions;*

Theoretical Chemisry – I

O-234

ADJUSTING ELECTRONIC STRUCTURE AND CONDUCTIVE PROPERTIES OF LI3N VIA PHOSPHORUS AND ARSENIC SUBSTITUTION

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Lithium nitrides have emerged as promising anode materials in lithium recharged batteries. The effect of phosphorus and arsenic substitution on electronic structure and conductive properties of Li$_3$N is investigated based on first-principles density functional theory within the generalized gradient approximation as implemented in the Vienna *Ab-initio* Package (VASP). The Li(2) site vacancy is found to be the dominant defect with the lowest formation energy under nitrogen-rich conditions. Vacancy formation brings about delocalization of valence electrons to increase electronic conduction. Partial P and As substitution reduces Li vacancy formation energy with inappreciable discrepancy of electronic structure, which suggests an improvement in Li ionic conduction. However, a full substitution of P and As for N results in variation of crystal structure from the space group *P6/mmm* to $P6_3/mmm$, and the energy band gaps of Li$_3$P and Li$_3$As are reduced to 0.72 eV and 0.65 eV respectively in comparison with 1.14 eV of Li$_3$N, which implicates an enhancement of electronic conduction. A full substitution also brings about an increase of Li vacancy formation energies, suggesting degradation in Li ionic conduction. Therefore, our calculations suggest that it would be viable to achieve balanced electronic and ionic conduction of Li$_3$N by controlled P and As substitution. It provides instructive information for experimental researches on synthesizing ternary lithium nitride compounds with designed electrochemical properties.

Keywords: *electronic structure; vacancy formation; ionic conduction; lithium nitride; structure variation;*

Theoretical Chemisry – I

O-235

IMPORTANCE OF VAN DER WAALS FORCES TO SURFACE STUDIES

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Dispersion interactions are ubiquitous in nature and contribute to the binding in biomolecules, the adsorption of molecules on surfaces, and the condensed phases of water, to name but a few. However, due to their non-locality and small magnitude, they are difficult to describe accurately by electronic structure methods. For example, density functional theory (DFT) with standard functionals can give misleading results for systems where dispersion is important. The van der Waals density functional (vdW-DF) of Dion et al. [Dion et al., Phys. Rev. Lett. 92, 246401 (2004)] is one of several promising approaches for accounting for dispersion. We have shown recently that with an improved treatment of the exchange part it can offer much better than chemical accuracy for a range of weakly interacting molecular systems [Klimes et al., J. Phys.: Cond. Matt. 22, 022201 (2010)]. Here we will show applications of the method to systems which are not in the weakly bonded regime such as solids and molecules adsorbed on solid surfaces. We show that in some cases, including dispersion turns out to be crucial to reconcile theory with the experiment, for example for water adsorption on metals [Carrasco et al., Phys. Rev. Lett. 106, 026101 (2011)].

Keywords: *Density functional calculations; Adsorption; Solid-state structures; Hydrogen bonds;*

Theoretical Chemisry – II

O-236

QM/CLASSICAL METHODS TO DESCRIBE PROPERTIES AND PROCESSES OF EXCITED STATES IN COMPLEX ENVIRONMENTS

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Nowadays molecular systems in their excited states play a fundamental role in many fields of science. In most cases, their photochemistry and photophysics are strongly affected, if not entirely determined, by the surrounding environment. For this reason, the accurate modelling of their properties, and of the phenomena and processes they undergo, requires to integrate proper quantum-mechanical (QM) descriptions with models which take into account the effects of the environment. In this talk, it will be shown that models based on hybrid QM/classical descriptions (either continuum or discrete) represent a valid computational strategy but only if mutual polarization effects between the QM and the classical part are possible and all the main physical specificities of the environment are properly taken into account. Examples of applications of these methods to phenomena involving molecular excited states (absorption, emission and energy transfer) in the presence of environments of increasing complexity will be presented and discussed.

Keywords: *Solvent effects; Quantum Chemistry; Energy transfer; Photophysics; Computational chemistry;*

Theoretical Chemisry – II

O-237

TOWARDS A DETAILED COMBUSTION MODEL FOR FURAN AND ITS DERIVATIVES THROUGH THEORETICAL STUDY OF THEIR H-ABSTRACTION RATE CONSTANTS

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The scarcities of fossil fuels in the transportation sector have motivated the interest in search of potential alternative reliable energy resources. An important alternative is to use biomass derived fuels as they are both renewable and have the potency to reduce pollutant emissions. Furan based biofuels (furanics) have been proposed as promising alternative fuels and studies to develop detailed kinetic models of their combustion are ongoing. The main consumption of these fuels in combustion processes is initiated by abstraction of a hydrogen-atom. Our first objective is to determine the rate coefficients of H-abstraction reactions from furanics by OH and HO_2 accurately. Therefore, the present work focuses on the computational investigation at DFT and G3B3 level of theories from 200-2000 K through canonical transition state theory incorporating Wigner's and Eckart's symmetrical and unsymmetrical tunneling corrections in order to calculate highly accurate Arrhenius parameters for these abstraction reactions.

The accurate abstraction rate expressions will be applied to construct a detailed combustion model for the furanics. The model development relies on both our detailed theoretical calculations for the abstractions as well as literature data and estimations for other reaction classes to construct the mechanism starting from an elaborate C_0-C_4 base chemistry set. The detailed kinetic model is validated against auto-ignition time results over wide temperature and pressure range for the fuels of interest. These experiments have been performed in our group within the cluster of excellence "Tailor made fuels from biomass" at the RWTH Aachen using a high-pressure shock tube and rapid compression machine. The goal of the model development is to capture and explain the interesting ignition chemistry observed at low to intermediate combustion temperatures of relevance to new engine concepts such as HCCI. The final combustion models will be applied for engine simulations for these novel fuels.

Keywords: *kinetics; ab initio calculations;*

Theoretical Chemisry – II

O-238

THEORETICAL STUDY FOR LITHIUM DIFFUSION IN SOLID STATE MATERIALS

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Lithium diffusion in lithium containing transition element disulphide and fluoride is investigated theoretically with periodic quantum-chemical methods. The calculated lithiation energies for the hexagonal titanium disulphide (h-Li_xTiS_2, x = 0.88,1.0) confirm that Li preferentially occupies the octahedral site rather than the tetrahedral site. Among the considered point defects, V_{Li}, V_{Ti}, and Ti_i, Li point defects are thermodynamically preferred in h-Li_xTiS_2. Competing pathways for Li diffusion in

h-Li_xTiS_2 are investigated using the climbing-image Nudged-Elastic-Band (cNEB) approach. Li^+ ions can migrate within the crystallographic *ab* plane either in a direct pathway through shared edges of neighboring octahedra or via vacant tetrahedral sites. The possibility of three-dimensional Li^+ diffusion along the *c* direction is investigated via inclusion of Ti point defects and Ti Frenkel defects. The calculated energetic properties show that ferromagnetic phase is more stable than the anti-ferromagnetic phase of lithium vanadium fluoride (α-Li_3VF_6). Three different inequivalent Li sites (Li(1), Li(2) and Li(3)) are observed where Li(1) occupies the middle position of the triplet Li(2)–Li(1)–Li(3). The calculated Li vacancy formation energy shows that vacancy formation at the Li(1) and Li(3) sites are easier than that in Li(2) site. The Li exchange processes between Li(1) to Li(3), Li(1) to Li(2) and Li(2) to Li(3) are studied by calculating the Li^+ migration between various sites. It is observed that Li exchange in α-Li_3VF_6 may take place in the following order: Li(1) to Li(3) > (Li(1) to Li(2) > Li(2) to Li(3). This is in well accord with the available experiment.

Keywords: *Lithium titanium disulphide; Lithium vanadium fluoride; Defects; Li Ion Diffusion; Activation energy;*

Theoretical Chemisry – III

O-239

THEORETICAL STUDIES OF ENZYMATIC REACTIONS

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Combined quantum mechanical/molecular mechanical (QM/MM) approaches have emerged as the method of choice for treating local electronic events in large molecular systems, for example, chemical reactions in enzymes or photoinduced processes in biomolecules. The lecture will outline the theoretical background and commonly chosen strategies for QM/MM studies of biomolecular reactions.[1–3] It will then describe some of our recent work on biocatalysis by enzymes which includes mechanistic studies on cytochrome P450cam,[4, 5] xanthine oxidases[6, 7], cyclohexanone monooxygenase (CHMO)[8], and glycosyltransferases (LgtC)[9]. These studies have addressed, inter alia, the competition between coupling and uncoupling reactions in the wild-type P450cam enzyme and its mutants, the crucial role of active-site residues in the reductive half-reaction of xanthine oxidases, the origin of enantioselectivity in CHMO-catalyzed reactions, and the favored reaction mechanism in LgtC. The examples presented will illustrate the chemical insights and the improved mechanistic understanding of enzymatic reactions that can be provided by QM/MM calculations.

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Keywords: *QM/MM; reaction mechanisms; enzymes;*

Theoretical Chemisry – III

O-240

OPTICAL PROPERTIES AND ULTRAFAST DYNAMICS OF PORPHYRIN ARRAYS

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Multiporphyrin arrays represent ideal building blocks for optoelectronic and light-harvesting materials since they can be produced in different shapes including oligomers and two-dimensional polymers. Great variability of possible multiporphyrin arrays allows to tailor their optical properties. We present here the theoretical study of the optical properties and ultrafast dynamics of different classes of porphyrin oligomers. We assign the optical spectra of these systems by using semi-empirical multi-reference and configuration interaction (MR-CI) method. Furthermore, we investigate the influence of specifically designed charged ligands on the optical absorption and the optical band gap of porphyrin oligomers. Since the functionality of optoelectronic and light-harvesting materials is determined by the interplay between the radiative and nonradiative relaxation processes, we perform surface hopping simulations of the ultrafast dynamics in order to determine the mechanism of the excited state relaxation in porphyrin oligomers.

Keywords: Molecular dynamics; Porphyrinoids;

Theoretical Chemisry – III

O-241

STOCHASTIC KINETIC MODELING OF THE SOAI REACTION

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The Soai reaction, which involves carbon-carbon bond formation using an organozinc reagent, is the best known example of absolute asymmetric synthesis[1]. In this presentation, it will be demonstrated how the experimentally observed distribution of enantiomers in the Soai reaction can be interpreted based on a chemical mechanism using a newly developed stochastic kinetic method, accelerated Monte Carlo simulation combined with deterministic continuation and symmetrization. The method is in principle suitable for handling large mechanisms with realistic particle numbers and could be useful for any case where the kinetics of a process shows inherent random fluctuations. The mechanism shows how a slow initial reaction combined with efficient and highly enantioselective autocatalysis can give rise to chiral symmetry breaking under completely nonchiral external conditions[2].

Acknowledgement: *This work was supported by the TÁMOP 4.2.1/B-09/1/KONV-2010-0007 project, which is co-financed by the European Union and the European Social Fund.*

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Keywords: *Kinetics; Asymmetric amplification; Autocatalysis; Enantioselectivity; Chirality;*

Theoretical Chemisry – III

O-242

AN IR AND DFT STUDY OF AMMONIA INTERACTION WITH FOSSIL PATTERN IN KBR MATRIX

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The role of ammonia in biological processes is not quite clear yet. Nevertheless in the last years the interest to the interaction of ammonia and fossil patterns is becoming immense. The problem of ammonia action in nature is connected in the first regard with the possibility of complex formation as an initial step in molecular transformation.The presented work the mechanism of appearance and structure of ammonia intermediates with water, cellulose acetate and betuline, employing IR experimental and DFT theoretical approaches is presenting.Usually the unstable adducts are fixed in the low temperature films. We have suggested a new variant of spectral method, using the stabilization of intermediates in KBr-matrix. The mentioned experimental tactic permits to investigate the complexes and their conversion at normal conditions. In this way we have revealed in IR-spectra of KBr-pallets, saturated by ammonia/water mixture before the pressing,in 3600-3000cm^{-1}and 1600-1400cm^{-1}region the new bands, which can be assigned to the water intermediates and ammonium cation vibrations. The experiments have shown that both weak water complexes and hydroxonium adducts can be stabilized in KBr-matrix. These data can be considered to some extent as the evidence of hydrogen transfer from water to ammonia molecule. At the interaction of cellulose acetate and ammonia it was established the existance of ammonia adducts with cellulose pattern in KBr-matrix. However for this system the hydrogen transfer between coupled molecules is not observed. In the case of betuline/ammonia system the IR-study indicates the hydrogen transfer in the intermediates of both betuline and ammonia.

The conducted DFT-calculations in terms of GAUSSIAN procedure have manifested the complex formation in the presented systems. We have considered different species of intermediates, including the varied ratio of components.The calculated frequencies agree well with the experimental values in general.

Acknowledgments: *This work has been financially supported by Russia Foundation of Basic Research (11-08-00707)*

Keywords: *ammonia; cellulose acetate; betuline; hydrogen bones; IR-spectroscopy;*

Theoretical Chemisry – III

O-243

CAR-PARRINELLO MOLECULAR DYNAMICS SIMULATIONS WITH GRIMME VDW CORRECTION FOR CLATHRATE HYDRATES CONSISTING OF ALCOHOL AND FLUOROCARBON MOLECULES

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Clathrate hydrates are crystalline compounds consisting of hydrogen-bonded water molecules forming cages that enclose guest molecules. Clathrate hydrates are expected to be used in transport of natural gas, storage of unstable molecules, and future energy resource. Since the phase equilibrium conditions of the clathrate hydrates are significant for these applications, variety of experimental measurements and theoretical studies have been performed to understand the stability of the hydrate phases. Although many guest substances are known to form hydrates, alcohol and fluorocarbon molecules are most important ones. Recently, several alcohol and halogenated hydrocarbon molecules such as ethanol, butanol, fluorocarbons are reported as promoters for hydrate formation. However, in the previous understanding, the guest molecules that have large dipole moment and coulomb interactions between cage water molecules like methanol are known as inhibitor for hydrate. Therefore the mechanisms of the stabilizations of hydrate phase by the alcohol and halogenated hydrocarbon molecules that have large dipole moments are still missing. Furtherer understanding of the effect for phase equilibrium conditions from the interactions between the guest and cage water molecules is important for future applications of clathrate hydrates.

The ab initio molecular dynamics simulation is a suitable way to observe the molecular behavior of the guest molecules in the hydrates. We performed Car-Parrinello MD simulation with vdW correction based on the Grimme model for the alcohol hydrates and fluorocarbon hydrates to calculate molecular motions of guest in the cages. As result, the hydrogen-bonding between guest and water molecules were observed and the vibrational spectrum was changed for alcohol hydrate. The differences of the molecular motions of fluorocarbons were also reported. The CH2F2 and CHF3 molecule moved along the long axis in the 51262 cages.

Keywords: *Inclusion compounds; Molecular dynamics; Ab initio calculations; Vibrational spectroscopy;*

Computational Chemistry – I

O-392

THE VALENCE BOND WAY IN CHEMISTRY

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"*Give us insight, not numbers*" was Coulson's admonition to theoretical chemists. My talk will show that Valence Bond (VB) theory provides insight and good numbers, and creates a great deal of order in Chemistry [1, 2]. In this talk I will show its application to bioinorgnic and organic chemisry. Potentially, if time permits, I may cover the following two stories:

(**a**) The first story concerns the reactivity of the iron-oxo species of Cytochrome P450 in H-abstraction, sulfoxidation, and aromatic hydroxylation, and how VB theory creates order and makes predictions in this complex field [1]. I will further teach how the VB model enables one to estimate H-abstraction barriers for reactions that range from $H+H_2$ to the etard reaction, permanganate oxidation, and all the way to Cytochrome P450 oxidation. A bridge will be created between normal hydrogen atom abstraction (HAT) and the proton coupled electron transfer (PCET) mechanism [1].

(**b**) The story of the oxy complexes of Myoglobin and Hemoglobin ($Mb.O_2$; $Hb.O_2$), which were "discovered" about 333 years ago, and their bonding features, which were outlined first in 1936, remain disputed for 75 years. We shall see how VB theory resolves the dispute by transforming the CASSCF/MM wave function to a VB/MM wave function, which shows clearly the bonding mechanism of O_2 to the ferrous heme complex [2].

It will be argued that VB theory and VB reading of the wave function is a productive future paradigm in chemistry.

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Keywords: *ab initio calculations; bioinorganic chemistry; C-H activation; iron; molecular modeling;*

Computational Chemistry – I

O-393

DYOTROPIC AND DOUBLE GROUP TRANSFER REACTIONS: ORIGINS OF THE REACTION BARRIERS

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Double group transfer (DGT) reactions are a general class of pericyclic reactions that occur through the simultaneous migration of two atoms or groups from one compound to another in a concerted reaction pathway.[1] The process is suprafacial on both reaction sites and therefore these $[\sigma 2_s+\sigma 2_s+\pi 2_s]$ transformations may be considered to be a thermally allowed pericyclic reaction according to the Woodward–Hoffmann rules. Strikingly, DGT reactions share a common feature, namely, they proceed in a concerted and synchronous fashion through a transition state featuring a six-membered ring that is highly in-plane aromatic.[2]

Despite the aromatic character of these transition states, DGT reactions are associated with relatively high barriers. The origins of these barrier heights have been studied with the help of the so-called Activation Strain Model. We found that, similar to other pericyclic processes, the activation strain associated with the structural rearrangement of the reactants is also the controlling factor for the high energy of the DGT reaction barriers.[3] In addition, the origins of the reaction barriers of related dyotropic reactions shall be also discussed.[4]

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Keywords: *Pericyclic Reaction; Reaction Mechamisms; aromaticity; Computational Chemistry;*

Computational Chemistry – I

O-394

THEORETICAL CHARACTERIZATION AND IDENTIFICATION OF ELECTRIDES

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The electrides[1-2] are intriguing chemical species with an electron not formally assigned to any atom. This situation is, however, completely different to that given in a metal where the electrons are delocalized between positively charged metal ions. The electron in an electride acts as a formal anion, which is bonded to positively charged species in the molecule. This particular feature of electrides prompts very particular chemical and physical properties: they are powerful reducing reagents, exhibit exalted electric linear and non-linear optical properties as well as a particular magnetic behavior.

In this work, we analyze the electronic structure and the identification of several electride structures by means of the Quantum Theory of Atoms in Molecules (QTAIM) and the Electron Localization Function (ELF).[3] Our results show that these tools make possible the classification of candidate species as electrides or not. It was already proved that one could distinguish the electride behavior in insulating high-pressure forms of alkali metals from ELF analysis[4] but now we show that with QTAIM and ELF is possible to characterize the electride behavior in all sorts of molecules.

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Keywords: *electronic structure; ELF; Nonlinear optics; bond theory; Density functional calculations;*

Computational Chemistry – I

O-395

UNDERSTANDING THE DIFFUSION OF SMALL GASES THROUGH POROUS ORGANIC CAGE NANOCRYSTALS VIA MOLECULAR DYNAMICS

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Most organic molecules pack in such a way to minimise free space therefore exhibiting minimal void volume and hence permanent porosity is rare. However, previously we have shown that tetrahedral organic cages can be synthesized and then desolvated to generate porous crystals that adsorb small guest molecules such as nitrogen, hydrogen, methane and carbon dioxide.[1] We have also shown that it is possible to control the particle size of these systems by altering the building blocks used within the makeup of the material.[2] These all exhibit a 3D-diamondoid pore network and by altering the modulus there is an impact on the pore size; as a result the diffusion of gases through them changes.

Upon the generation of a bespoke force field, it has been possible to simulate how the diffusion of small gases alter dependant on their particle size. Using molecular dynamic simulations we have unlocked phenomena such as gas selectivity, rare-event hopping and displacement of gases to regions previously considered inaccessible; all of which help to rationalize experimental observations. The aim here is to predict materials which show good selectivity to one gas over another.

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Keywords: *Molecular dynamics; Nanostructures; Microporous materials; Cage compounds; Computational chemistry;*

Computational Chemistry – II

O-396

HOW TO TREAT EXCITED STATES OF BIOMOLECULES

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For the UV/Visible absorption of molecules in the gas phase, the Franck-Condon principle is very often invoked. It states that, the electronic motion being so fast compared to the nuclear motion, the molecular geometry can be considered fixed.

In solution, the geometry of the chromophore is still considered unchanged during the absorption process, but the internal geometry of solvent molecule and their relative orientations also. A contrario, the electrons of the solvent molecules can react instantaneously to the modification of the electronic cloud of the chromophore. This is called the electronic response of the surrounding (ERS). A solvent is generally an isotropic media, in average, that can be modeled by a polarizable continuum characterized by the relative dielectric constant with separated electronic and nuclear contributions. Hence, extracting the electronic contribution is trivial in so called self-consistent reaction field approaches (SCRF).

Oppositely, macromolecules need an atomic description using hybrid methods combining quantum mechanics and molecular mechanics (QM/MM). Usual force fields, describing the surrounding of the chromophore, consider atoms as a whole and do not explicitly consider the electrons. This clearly prevents the ERS to be taken into account. Instead of using polarizable force fields, we propose a simple method which combines hybrid QM/MM techniques with SCRF approaches to evaluate the ERS in macromolecules. This method will be detailed and applied to the interpretation of the absorption spectra of various systems of biological interest.

In addition, a modification of the QM/MM method we developed will be presented in order to avoid spurious excitations.

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Keywords: *QM/MM; excited state; polarization;*

Computational Chemistry – II

O-397

THERMAL ISOMERIZATION OF COMPOUNDS FROM THE PINANE SERIES AS MODEL SYSTEMS FOR KINETIC STUDY AND MODELLING OF SUBSTITUENT EFFECTS

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Monoterpenes and Monoterpenoids from the pinane series are interesting compounds for the study of structural influences of the reaction kinetics. The thermal isomerization of those compounds is not only from scientific interest but also from industrial importance since products arising from the reactions are valuable intermediates for fine and specialty chemicals. For instance the pyrolysis of β-pinene affords via ring-opening of a strained vinylcyclobutane-system myrcene, a valuable building block for Vitamin E and A precursors as well as for industrial synthesis of carotinoids. The bottleneck in those processes is the thermal rearrangement, since different parallel reaction channels affording a series of products. Fundamental understanding of the reaction kinetics as well as of the elementary steps going on are from importance for an industrial application of such reactions.

Therefore, the thermal isomerization of α-pinene, β-pinene, pinane, and pinan-2-ol has been studied using a flow type apparatus allowing the performance of the reactions in the gas phase with nitrogen as carrier and diluting gas. Kinetic analysis of the experimental results allowed for the identification of individual reaction pathways, whereas the product distribution strongly correlates with the structural entities of the bicyclic starting molecules. Additionally, the reactivity of the molecules depend on the occurrence of vinylcyclobutane or cyclobutane substructures in the bicyclic carbon skeleton. The starting materials can be rearranged via biradical intermediates to either acyclic reaction products ([2+2] cycloreversion) or monocyclic isomers ([1,5]*H* shift). The first type of reaction products is able to undergo rearrangement to cyclopentanes derivatives following an Ene-type cyclization mechanism. Reaction mechanism is supported by computational studies and kinetic models allow the prediction of experimental conditions leading to high yields of the target products.

Keywords: *Rearrangement; Gas-phase chemistry; Kinetic modelling; Reaction mechanism; Computational study;*

Computational Chemistry – II

O-398

QUANTUM-CHEMICAL STUDY OF THE REACTION MECHANISM OF POLYPEPTIDE UDP-GALNAC TRANSFERASE 2, A RETAINING GLYCOSYLTRANSFERASE

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Glycosylation of cell surface proteins plays a crucial role in cell communication and recognition. Alterations in glycan structures are linked to many diseases with the most prominent example being cancer. To understand the regulation of glycosylation and to be able to modify it, reaction mechanisms of involved glycosyltransferases have to be known. However, reaction mechanism of the configuration-retaining group of glycosyltransferases hasn't been sufficiently explained yet.

For this reason we have chosen a retaining glycosyltransferase – polypeptide UDP-GalNAc transferase (ppGalNAcT) – as the subject of our quantum-chemical study. This enzyme catalyses the transfer of N-acetylgalactosamine moiety onto serine or threonine hydroxyls, forming the first bond of the so-called O-linked glycosylation pathway. Increased activity of ppGalNAcT has been found to enable metastasis of breast and colorectal cancer.

We're studying human ppGalNAcT2 by a hybrid QM/MM approach using density functional theory for the important part of the active site. We have found that the commonly used Becke-Perdew functional completely fails to describe the shape of the potential energy surface, while the OPBE functional provides results in good agreement with state-of-the-art meta-hybrid functional M06-2X. Structures of reactant and product have been successfully obtained on the OPBE-D3/TZP level, enabling a 2D potential energy surface scan to locate the transition state candidates for final optimisation. Results suggest that the reaction proceeds via a one-step S_Ni mechanism, initiated by proton transfer from acceptor hydroxyl to donor phosphate. This conclusion agrees well with recent experimental evidence.

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Keywords: *glycosylation; reaction mechanisms; quantum chemistry; transferases; density functional calculations;*

Computational Chemistry – III

O-399

OXIDES FILMS AT THE NANOSCALE: NEW STRUCTURES, NEW FUNCTIONS AND NEW MATERIALS

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SiO_2 films of few nanometers thickness have been the basis of the microelectronics revolution but ultrathin oxide films grown on a metal have a wide range of properties and applications [1]. They are essential to confer a specific property to a material (biocompatibility of titania implants in medical applications via formation of a thin titania layer, corrosion protection of metals by passive layers) or are fabricated in devices especially designed to exploit the reduced thickness of the oxide layer (e.g. tunneling magnetoresistance sensors, solar energy materials, ferroelectric ultrathin film capacitors). Oxides at the nanoscale may exhibit specific surface morphology, physical properties, chemical reactivity, thus providing new opportunities for the design of innovative materials. Theory has a very important role in this field and can answer several important questions. Are the electronic properties of an oxide film of just a few atomic layers similar to those of the corresponding bulk material? How important is the formation of a metal/oxide interface for the surface properties? What is the role of the strain in the epilayer? How thick an oxide film has be to recover typical bulk properties? Are the nature of the defects and even the chemical composition of the film similar to those of the bulk crystalline phase? These and other related questions will be addressed in this talk by discussing transport phenomena across the ultrathin insulating oxide barrier (charging effects), the structural flexibility of oxide ultrathin films and their relevance in catalytic processes, nanoporosity and the possibility to stabilize atomic species at the metal/oxide interface, change in electronic properties by selective doping of oxide nanostructures [2].

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Computational Chemistry – III

O-400

THE FROZEN CAGE MODEL: A COMPUTATIONALLY LOW-COST TOOL FOR PREDICTING THE EXOHEDRAL REGIOSELECTIVITY OF CYCLOADDITION REACTIONS INVOLVING ENDOHEDRAL METALLOFULLERENES

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Functionalization of endohedral metallofullerenes (EMFs) is an active line of research that is important for obtaining nanomaterials with unique properties that might be used in a variety of fields, ranging from molecular electronics to biomedical applications. Such functionalization is commonly achieved by means of cycloaddition reactions. The scarcity of both experimental and theoretical studies analyzing the exohedral regioselectivity of cycloaddition reactions involving EMFs translates into a poor understanding of the EMF reactivity. From a theoretical point of view, the main obstacle is the high computational cost associated with this kind of studies. To alleviate the situation, we propose an approach named Frozen Cage Model (FCM).[1] The FCM represents a fast and computationally inexpensive manner to perform accurate qualitative predictions of the exohedral regioselectivity of cycloaddition reactions in EMFs. The Diels-Alder (DA) cycloaddition of 1,3-*cis*-butadiene to $X@D_{3h}$-C_{78} ($X=Ti_2C_2$,[2] Sc_3N,[3] and Y_3N[4]) EMFs provides a justification of the method. Moreover, the efficiency and successfully of the FCM is corroborated by the regioselectivity prediction of the DA addition of 1,3-*cis*-butadiene over all $X@I_h$-C_{80} ($X=Sc_3N$, Lu_3N, Y_3N, Y_3, Sc_3NC, Sc_3C_2, Sc_4O_2, Sc_3CH, Sc_4O_3, Sc_4C_2, La_2, and Ce_2) EMFs species synthesized until nowadays.[5]

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Keywords: *Regioselectivity; fullerenes; cycloadditions; Density functional calculations; Cage compounds;*

Computational Chemistry – III

O-401

OXIDATION OF ALKANES: IN SILICO CATALYST DESIGN

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Alkane C-H activation, and in particular, selective oxidation under mild conditions has been an enduring challenge in catalysis. In an effort to match the *in vivo* effectiveness of metallo-enzymes such as cytochrome P-450, much attention has been drawn to metal-oxo systems that can mimic their reactivity.[1] The selective oxidation of alkanes into various oxidized products employing a transition metal catalyst together with the oxidative agent (i.e. hydrogen peroxide in Fenton chemistry processes) has been thoroughly investigated by computational means.[2] Various metal-centred catalysts have been proposed for the above functionalization ranging from $[FeO(H_2O)_5]^{2+}$ and the ammonia substituted equivalent[2, 3] to Mn-heme containing systems.[4] A plausible mechanism that governs the C-H bond activation is the oxygen rebound mechanism[5] which applies to remarkably diverse systems.

Theory can assist in tailoring an efficient catalyst, finding the optimum compromise between a fast H-abstraction/O-rebound step but also a facile regeneration of the iron-oxo active site. The latter part of the catalytic cycle is often neglected in the literature but represents a determining factor for the functionality of the catalyst. In the present DFT study, the complete catalytic cycle is considered, so that complexes that are known to perform well in the H-abstraction/O-rebound step are also assessed at the regeneration step. Heme and non-heme containing systems such as the ones mentioned above are included in the study. Furthermore, the effect of the equatorial or axial position of the ligands on the spin state and reactivity of the species is also taken into account, throughout the catalytic cycle.

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Keywords: *C-H activation; Density Functional Calculations; Homogeneous Catalysis;*

Computational Chemistry – III

O-402

BRIDGES BETWEEN THE PHYSICS AND CHEMISTRY OF MOLECULAR CONDUCTORS

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Molecular conductors are low-dimensional materials at the crossroads of chemistry and physics. They offer fertile ground where new ideas from the two disciplines can be brought together to induce new phenomena or test new concepts. To have some control over their properties it is advisable to understand their electronic structure which provides the simplest link between the chemical nature and the physical properties. These solids are usually build from two different sublattices put together to induce conducting properties in one of them.

Although simple tight-binding approaches have been extremely successful in understanding many aspects of the electronic structure of these solids, some features require a more precise evaluation for a comparison with experimental results to be meaningful. Accurate first-principles density-functional theory (DFT) calculations are now possible for systems with large and complex unit cells like many molecular conductors. However, to fully exploit this potential, chemically oriented ways to analyze the results are needed. In this presentation we will report the results of DFT calculations using localized basis sets, which are very well suited for this goal, for several of these solids.

Systems to be discussed include alpha-type BEDT-TTF conductors and Bechgaard salts. Despite the fact that these salts have been intensely studied for longtime some quite fundamental aspects of their physical behavior are still not well understood. In particular, we will discuss the origin of the low-temperature modulation exhibited by alpha-$(BEDT\text{-}TTF)_2KHg(SCN)_4$ and the charge-ordering transition in alpha-$(BEDT\text{-}TTF)_2I_3$ both of which are associated with anomalies in their electrical conductivity. The interaction of the conducting properties of one of the two sublattices with other properties of the remaining sublattice will also be considered.

Keywords: *Electronic Structure; Conducting Materials; Density Functional Calculations; Materials Science; Electronic Transport;*

Computational Chemistry – IV

O-403

TUNING CATALYTIC REACTIVITY ON METAL AND OXIDE SURFACES: INSIGHTS FROM DFT

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Tuning catalytic reactivity by atomic scale modifications of the catalyst's surface is a key aspect of fundamental catalysis. In this lecture we will present and compare insights obtained from DFT calculations on metal and oxide surfaces.

The first example will deal with the modification of Pt by alloying. Mixing with Sn forms a PtSn surface alloy, decreasing the reactivity of the Pt atoms, especially with C and H atoms. This weakening has a direct influence on the selectivity for the hydrogenation of unsaturated aldehydes by lowering the adsorption energy of unsaturated alcohol, and allowing its desorption from the catalyst.[1] In the case of butadiene selective hydrogenation, the lower Pt-C interaction opens a new hydrogenation pathway, where the C=C bond to be hydrogenated in not coordinated to the surface.[2] This strongly reduces the barrier for the selective pathways towards butene formation.[3]

The second example will deal with the influence of coadsorbates on the surface, and we will focus on H_2O and OH groups. On alumina, water can have a beneficial effect by increasing the basicity of surface O atoms, hence favouring the surface reactivity for methane or H_2 dissociation.[4] On a Rh or Pt surface, OH groups form strong hydrogen bonds with alcohol reactants, rendering OH activation easier, but disfavouring C-H bond breaking [5, 6]

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Keywords: *heterogeneous catalysis; surface chemistry; reaction pathways; Density Functional Theory;*

Structural research for tomorrow

O-500

MICROSCOPIC INSIGHTS ON CHEMICAL STATE AND MORPHOLOGY OF KEY COMPONENTS IN OPERATING MODEL FUEL CELLS USING SYNCHROTRON-BASED METHODS

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Fuel cells are one of the most appealing environmentally friendly devices for effective conversion of chemical energy into electricity and heat, but still there are key barriers to their broad commercialization. Along with efficiency a major challenge of fuel cell technology is durability of the key components (interconnects, electrodes and electrolytes) that can be subject of corrosion or undesired morphology and chemical changes occurring under operating conditions. The complementary capabilities of synchrotron-based x-ray microscopes in terms of imaging, spectroscopy, spatial and time resolution and variable probing depths have opened unique opportunities to explore the structure and chemical composition of these technologically relevant complex materials and correlate them to the actual operating conditions.[1, 2] The most recent achievements in this respect, which are prerequisite for understanding and controlling the performance and durability of such devices, will be illustrated by selected results obtained with simplified versions of proton exchange membrane fuel cells (PEMFC) [3] and solid oxide fuel cell (SOFC)[4]. The reported results will demonstrate in-situ monitoring of the red-ox reactions or side reactions resulting in undesired deposits at the interconnects and electrodes, interactions at the interfaces of the electrodes and electrolyte and release of corrosion products to the electrolyte phase of PEMFC, mass transport processes and structural changes occurring at the high operation temperatures of SOFC and promoted by the polarization.

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Keywords: *surface chemistry; electrochemistry; interfaces; x-ray absorption pectroscopy; photoelectron spectroscopy;*

Structural research for tomorrow

O-501

VOLUMETRIC PROPERTIES OF SOME ALIPHATIC MONO AND DICARBOXYLIC ACIDS AND THEIR SODIUM SALTS IN WATER AT 298.15 K

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On the base of densimetric measurements the apparent molar volumes of aliphatic carboxylic acids of the type: $H(CH_2)_nCOOH$ [n = 1– 8] and $(CH_2)_n(COOH)_2$ [n = 0 – 6], sodium salts of saturated aliphatic carboxylic acids of the type: $H(CH_2)$,COONa [n = 1– 8], $(CH_2)_n(COONa)_2$ [n = 1– 8] and $Cl(CH_2)_nCOONa$ [n = 1– 4], sodium salts of unsaturated aliphatic acids of $H(CH_2)_{n-2}CH{=}CHCOONa$ [n = 2 – 7] and $CH_2{=}CH(CH_2)_{n-2}COONa$ [n = 2 – 4] types and monosodium salts of aliphatic dicarboxylic acids of the type: $HOOC(CH_2)_n(COOH)_2$ [n = 0– 6] in dilute aqueous solution were determined at T = 298.15 K. The density of studied solutions of electrolytes was measured at the concentration range $0.0050 \leq m / (mol \cdot kg^{-1}) \leq 0.3000$ using a vibrating-tube densimeter (DMA 5000, Anton Paar, Austria).Suggested by us modification of the equation describing the apparent molar volume, derived after taking into account all existing in a solution ions, undissociated molecules and all present here equilibria, allowed us to determine the limiting apparent molar volumes (partial molar volumes) of all anions and undissociated acids. In the case of salts of the NaHA type the entirely new method of determining the partial molar volume of HA^- anions was used based on treatment of a solution of monosodium salt as a mixture of different types of electrolytes. The variations of these values were analysed as a function of length of the aliphatic chain of studied electrolytes.

Keywords: *density; apparent molar volumes; carboxylic acid;*

Structural research for tomorrow

O-502

MOLECULAR MODELING OF ZNO NANOPARTICLE NUCLEATION: FROM PRE-NUCLEATION CLUSTERS TO FUNCTIONALIZED PARTICLES

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We demonstrate the molecular modeling of ion cluster formation, ripening reactions, nucleation and growth of zinc oxide nanomaterials. Key issues are the molecular mechanisms of self-organization, growth control and surface stabilization by surfactants. This is aiming at the fundamental understanding needed for the guided formation of nanostructures with tailor-made properties. Our simulation scheme (Kawska-Zahn method[1, 2]) allows to explore the evolution of a forming aggregate ion-by-ion. In doing so, the method combines Molecular Dynamics, Monte-Carlo and quantum/classical modeling to tackle the time/length-scale problem inherent to crystallization from solution[3]. At first we show the very initial steps of pre-nucleation cluster formation from Zn^{2+} and OH^-ions and $Zn_4O(OAc)_6$ precursors. The mechanistic insights include the emerging of transition clusters as well as the influence of counterions on the stability of the aggregates. Moreover, we present for $ZnO/Zn(OH)_2$ core/shell nanoparticles cluster ripening and nucleation of early wurtzite domains[4]. Exploring subsequent stages of particle growth for various crystal surfaces, we reveal the association and surfaces structure of organic molecules like carboxylates and amines. Eventually we propose mechanisms of stabilization and growth inhibition by those surfactants.

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Keywords: *Molecular dynamics; Nanoparticles; Surfactants;*

Structural research for tomorrow

O-503

QA OF DYE-SENSITIZED NIO NANOPARTICLE LAYERS VIA RESONANCE RAMAN MICROSPECTROSCOPY: DYE DESORPTION DYNAMICS IN WATER

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Dye-sensitized solar cells (DSC) have gained a significant scientific impact in the last years. State-of-the-art DSCs consist of a dye-sensitized nano-porous TiO_2 electrode and a passive counter-electrode (usually Pt).[1] Recently, efforts have been made to activate the cathode to build so-called tandem solar cells which achieve theoretically higher efficiencies. Promising materials are *p*-type semiconductors, e. g. NiO_x that exhibits an appropriate band position, is chemically stable and accessible.[2]

Monolayer and bilayer (2-step synthesis) NiO_x substrates are produced and sensitized with modified Ruthenium bipyridine dyes. In order to characterize the quality of these dye-sensitized NiO_x layers spectroscopic techniques such as UV-vis spectroscopy, luminescence spectroscopy, and resonance Raman (rR) microspectroscopy are applied. Thereby, it is possible to detail with rR microspectrsocopy the distribution of the dye on the surface and to map inhomogeneities or vacancies in the layer. Furthermore, a statistically profound analysis of the dye desorption dynamics upon addition of water, which influences the long-term stability of the solar cell, is performed. The desorption on the monolayer is faster than on the bilayer and the rR signal ratio of the dye on the monolayer compared with the bilayer changes from 1 to 2 without a washing step to about 1 to 5.8 after washing in water for 20 min. This change in ratio can be attributed to binding sites on the NiO_x surface that are passivated with regard to water penetration. These passivated "vaults" are introduced upon the second synthesis step that is needed to build the bilayer.

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Keywords: *Raman spectroscopy; Ruthenium; Laser spectroscopy; Vibrational spectroscopy; Nickel;*

Ultra Fast Processes – I

O-504

ULTRAFAST OPTICAL AND X-RAY STUDIES OF THE CHARGE, SPIN AND STRUCTURAL DYNAMICS IN SOLUTIONS

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We will present results of our studies of metal-based molecular complexes in solution. We will show how with a combination of ultrafast fluorescence up-conversion and ultrafast optical and X-ray absorption spectroscopy, and quantum chemical simulations, we have obtained a detailed description of the photocycle of Fe-based complexes, which implies a large spin transition (DS = 2) on an ultrafast time-scale (< 150 fs). We have recently implemented a new set-up for ultrafast 2 dimensional spectroscopy in the UV around 300 nm. we will show how this technique allows us to retrieve additional information about the relaxation dynamics in Fe-complexes. Finally, we will present our ultrafast fluorescence studies of metalloporphyrins yielding new insight into their relaxation pathways.

Keywords: *ultrafast; X-ray; solutions; structural dynamics;*

Ultra Fast Processes – I

O-505

ULTRAFAST DYNAMICS, COMPOSITION AND STRUCTURE OF CONFINED SYSTEMS TOWARDS 4D CHARACTERIZATION

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A correlation between a structure and a function is a well defined concept in biochemistry and it is clearly relevant also for other fields of natural sciences. However, there is a third component - a time domain. To determine the changing structure in real time is then of interest, especially on molecular level.

This contribution represents an attempt to provide a unique overlap between the dynamics in 1D time and the structural characterization in 3D along with the chemical composition. Our experiments are based on time-resolved laser fluorescence spectroscopy providing ultrafast dynamics, secondary ion mass spectrometry providing the chemical composition within 3D location, and atomic force microscopy providing topography and morphology of the structure surfaces.

The concept is discussed on two examples. The first is the double confined system of

coumarin C522 (C522) in aqueous solution of b-cyclodextrin and additionally in AOT (natrium dioctyl-sulphosuccinate) /n-heptane/water micelle. The micelle diameter is systematically changed. The dependence of the micelle diameter and presence of b-cyclodextrin on fluorescence dynamics is discussed. The second is a copolymer of dimethyl ester of 3,3````- bisdecyl [2,2`; 5`,2``; 5``,2```; 5```, 2````; 5````, 2`````] sexithiophene-5,5`````- dicarboxylic acid with polyethylene oxide. The film preparation reveals the differences in fluorescence dynamics supported by details of local composition and structure.

Keywords: *Femtochemistry; Mass spectrometry; Micelles; Cyclodextrins;*

Ultra Fast Processes – I

O-506

STRUCTURAL DYNAMICS OF COVALENT PERYLENE-BASED SYSTEMS PROBED WITH FEMTOSECOND STIMULATED RAMAN SPECTROSCOPY

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Understanding the charge transfer (CT) dynamics on the femtosecond to picosecond timescale provides crucial information to the development of bio-inspired photocatalytic systems for solar fuels and solar energy. For several donor-acceptor systems, the CT state remains a convolution of locally excited states (ES) or radical ion pairs, which prove difficult to understand using time resolved spectroscopy. However, spectroscopic techniques such as transient absorption give little useful information relaying structural information in the excited state and CT processes that occur on the fs to ps time scale. In order to obtain simultaneous high temporal and spectral resolution, it is necessary to have a structural probe with sub-picosecond time resolution. The recent development of femtosecond stimulated Raman spectroscopy (FSRS) enables observation of vibrational structural information with resolution comparable to vibrational dephasing times. FSRS also has the advantage of being insensitive to fluorescence, which can hinder the use of structural techniques such as spontaneous Raman spectroscopy for broadly used, solar-driven chromophores such as perylene diimide (PDI, $\varepsilon = 80{,}000\ M^{-1}\ cm^{-1}$).

We demonstrate the use of FSRS to elucidate ES and CT dynamics of various perylene-based chromophores. Here we present a study of picosecond vibrational dynamics of the CT and ES of perylene, PDI, and perylene monoimide (PMI). Evaluation of these chromophores reveals strong C=C core stretching vibrations that, though consistent in the ground state, vary significantly upon excitation to the first excited state, S^1. For instance, a strong, dispersive feature at 1593 cm^{-1} is solely present in the ES of PDI, suggesting the utilization of a new vibrational coordinate. Analysis of the photoreduced PDI anion in a dyadic system demonstrates significant contributions from these additional modes. Understanding the structural motion of different states will provide needed insight as we move to effectively design an efficient solar fuel.

Keywords: *Electron Transfer; Charge Transfer; Photophysics; Raman spectroscopy; Time-resolved Spectroscopy;*

Ultra Fast Processes – II

O-507

ULTRA-FAST LASER MATERIALS PROCESSING

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Femtosecond Nanoscale Processing is reviewed for a wide variety of representative material classes, such as metals, semiconductors, dielectrics, ceramics, polymers, and biopolymers. The photo-electronic excitation mechanisms of these materials are compared in terms of incubation phenomena and material-specific electronic behaviours[1, 2]. An increase of pulse duration and pulse repetition rate into the megahertz range yielded a rising contribution of thermal excitation. Non-thermal and thermal processes, which determine the extent of the heat-affected zones, could be identified during the ablation process. Laser-induced periodic surface structures depend on the pulse length, the laser fluence, the number of laser pulses, the polarization, and on the shape of temporally tailored pulses[3, 4]. New insights into such self-assembly phenomena induced by femtosecond laser treatment on solid materials were gained. Current work with optical-field enhancement and confinement for an asymmetrically illuminated nanoscopic SFM tip illuminated by fs-laser pulses suspended over different materials is shortly reported. Since the first fundamental femtosecond pulse laser ablation studies on human corneas[5], the use of sub-picosecond laser experienced vivid attention in surgery[6]. These processes involve non-linear optical coupling being highly dependent on the local intensity.

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Ultra Fast Processes – II

O-508

DEGENERATE FEMTOSECOND PUMP PROBE STUDIES OF LEAD SULFIDE NANOCRYSTALS AT THE BAND GAP

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One method of creating high efficiency third generation photovoltaics is to exploit carrier multiplication observed in narrow band gap light absorbers. Bi-exciton formation in different semiconductor quantum dots has been shown to occur when single photon excitation occurs via photons of energy 3 times the band gap or greater. The potential for carrier multiplication from photons at the peak of the solar spectrum, motivate the study of nanomaterials with band gaps between 0.6 to 1.2 eV in the near- and short-wave infrared. Femtosecond four-wave mixing in the short-wave infrared can be used to measure dynamics in both isolated colloidal quantum dots and, most importantly, coupled quantum dot arrays suitable for device applications. Disagreements exist about timescales for fundamental photophysical processes, such as carrier cooling and impact ionization: timescales reported in different studies vary from tens of femtoseconds to picoseconds. Degenerate pump-probe spectroscopy is used to investigate and compare relaxation times in arrays and colloidal solutions of lead sulfide quantum dots. The time-dependent behavior of different sizes of PbS nanocrystal arrays and solutions is measured at the respective band gaps with 25 fs to 85 fs time resolution.

Keywords: *quantum dots; ultrafast spectroscopy;*

Ultra Fast Processes – II

O-509

ROLE OF CHROMOPHORES ARRANGEMENT IN COHERENT ENERGY MIGRATION IN LIGHT-HARVESTING COMPLEXES

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The rapid development of two-dimensional electronic spectroscopy (2DES) has been central to the discovery of subtle quantum-coherent mechanisms in the natural light-harvesting process[1] as well as in artificial systems.[2] The role of such mechanisms in enhancing the efficiency of energy transfer (ET), although very appealing, is still not well understood. Moreover, still unknown are the factors regulating the presence of such effects although many theories have now been proposed about the role of structure and environment.[3]

From a practical perspective, the possibility of correlating the presence of quantum-coherent dynamics to special structural motifs would opens the door for the design of new molecular assemblies by exploiting quantum attributes built into the system Hamiltonian, essentially by the choice of the nature and the structural arrangement of chromophores.

With the aim of identifying if and which structural motifs play a major role in the coherent driving of energy migration, in this work two evolutionary-related light-harvesting proteins isolated from marine algae were studied by means of 2DES. The two complexes, named PC645 and PE555, are characterized by analogous structures but they present slight differences in the nature and in the arrangement of the absorbing chromophores. The measurements, performed at room temperature and physiologically relevant conditions, revealed for both complexes exceptionally long-lasting excitation oscillations with distinct anti-correlations, attributable to electronic quantum-coherences. The most interesting result is that, while in PC645 the quantum beating associated with electronic coherence lasts for at least 300 fs[1], in PE555 the anticorrelated beating was recorded for less than 100 fs. The differences in the coherent dynamics of the two complexes are tentatively discussed in terms of their structural differences.

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Ultra Fast Processes – II

O-510

GAS-SOLID-SHIFT IN MOLECULAR INNER-SHELL TRANSITIONS

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Clusters and nanoparticles are known to bridge the gap between the condensed and the gaseous state of matter. Inner-shell excitation has been shown earlier to be a suitable approach to probe size effects of matter. However, accurate comparisons of core-to-valence transitions between gaseous molecules and the corresponding condensed phase are scarce.

We present results on spectral changes that are observed between gaseous and condensed molecules in the inner-shell excitation regime. The experiments are carried out at the electron storage ring BESSY II (HZB Berlin). Condensed phase spectra are obtained from multilayers of condensed molecules. Gas phase spectra are simultaneously recorded, so that the energy scale is constant within 5 meV.

Specifically, the C 1s-π^* transition in benzene (C_6H_6) is studied where a red-shift by 60 meV is observed in the condensed phase relative to the gas phase spectrum. This spectral shift is slightly smaller than that observed earlier for free benzene clusters. These findings are discussed in the context of structural changes occurring between molecular solids and micro-clusters, which are studied by *ab initio* calculations.

Spectral shifts upon cluster formation in solution have also been observed in liquid microdroplets, when they reach supersaturation. These studies are performed in the hard X-ray regime, where the formation of Bjerrum pairs as well as solute clusters are formed in highly concentrated solutions. Structural information of such clusters is also inferred from model calculations.

Keywords: *clusters; X-ray absorption spectroscopy; nanoparticles;*

Ultra Fast Processes – II

O-511

EXCITED-STATE PROPERTIES IN PH-SWITCHABLE RUTHENIUM DYES

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Ruthenium polypyridine dyes are amongst the most studied compounds due to their unique combination of chemical stability and redox and optical properties, which are exploited in the design of e.g. artificial light-harvesting systems and molecular sensors. By incorporating extended ligand structures bearing basic/acidic positions, complex structures sensitive to environment pH can be designed. The resulting effects may be useful for pH-sensing applications and the design of pH-switchable optical devices. By de(protonation) the character of individual excited states is influenced, changing not only the absorption properties. Lifetimes of excited states and general decay mechanisms of the photoexcited structures may alter significantly.[1]

Here we present a series of pH-sensitive structures which were investigated combining experimental and theoretical approaches. Applying resonance Raman spectroscopy and DFT calculations a detailed picture of the initial excited states and the changes induced by (de)protonation is developed.[2] Additionally, a comparison of calculated and experimental absorption and resonance Raman spectra allows for unambiguous identification of the protonated species present at certain pH ranges, which is especially important in the case of multiple positions available for protonation.[3] Applying time-resolved transient absorption spectroscopy the interplay between relative energetic positions of excited states in dependence on the protonation state and the excite state decay mechanism is revealed.

Acknowledgement: *This work was financially supported by the Studienstiftung des deutschen Volkes (M.W.), the Fonds der Chemischen Industrie (B.D.) and the Thüringer Ministerium für Bildung, Wissenschaft und Kultur (Grant-No. B 514-09049, PhotoMIC).*

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Keywords: *Ruthenium; Photophysics; time-resolved spectroscopy; computational chemistry; protonation;*

Ultra Fast Processes – II

O-512

KINETIC DETERMINATION OF THE ALKYLATING POTENTIAL OF VINYL COMPOUNDS

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Humans are exposed to alkylating compounds present in the environment and also produced endogenously. Many of these compounds are mutagenic and genotoxic due to their ability to interact with proteins and DNA [Gates, K. S. *Chem. Res. Toxicol.* 2009,**22**, 1747]. The alkylating potential of four vinyl compounds (VC) was investigated: acrylamide (AM), acrylonitrile (AN), acrolein (AC) and acrylic acid (AA). As common substrate of alkylation, 4–(*p*–nitrobenzyl)pyridine (NBP) -that forms colored adducts with them- was used. These reactions occur through an enthalpy-controlled Michael addition mechanism, being moderately accelerated by electron-withdrawing groups. The sequence of alkylating potential was as follows: AN > AM > AA > AC.

The alkylating potentials of the same VC on the nucleosides guanosine (Guo) and uridine (Urd) were also investigated. A novel Ultra Fast Liquid Chromatography (UFLC) technique was used to monitor the alkylation reactions. The following conclusions were drawn: **i**) AC presents the higher alkylating potential, showing reaction over Guo and Urd at cellular pH, which support its biological importance [Feng, Z. *Proc. Natl. Acad. Sci. U.S.A.* 2006, **103**, 15404]; **ii**) the alkylation reactions of Urd and Guo by the UC occur through a Michael addition mechanism; **iii**) a correlation between chemical reactivity (alkylation rate constants and thermodynamic activation parameters) and mutagenicity was found; **iv**) The sequence of alkylating potential with the nucleosides was as follows: AC > AN > AM ~ AA; **v**) the coherence between the results obtained with the nucleosides and NBP allow one to consider NBP-test as a simple biomimetic assay with predictive character.

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Keywords: *alkylation; nucleosides; kinetics;*

Self-assembly, Molecular Recognition and Biomaterials – I

O-108

PLANT CYSTOLITHS: COMPLEX FUNCTIONAL BIOCOMPOSITES DESIGNED TO SCATTER LIGHT

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Plant cystoliths are mineralized objects formed by specialized cells in the leaves of certain plants. The main mineral component of cystoliths by volume is amorphous calcium carbonate (ACC), but a silica stalk, which is found to be essential for ACC formation, is always the first formed mineral. The cystolith is composed of four distinct mineral phases with different chemical properties: An initial silica phase blends into a Mg-rich silica phase, which in turn mediates the transition to a highly stable ACC phase. Encapsulating the first ACC phase, a bulky and less stable ACC phase is deposited. This complex architecture poses interesting questions not only about the strategy for ACC stabilization,[1–2] but also about the physiological function of the mineralized objects.

Cystoliths are regularly distributed in the epidermis of leaves and protrude into the photosynthetic tissue. The photosynthetic pigments generate a steep light gradient in the leaf. Under most illumination regimes the outer leaf layer is light saturated, thus the photosynthetic apparatus is kinetically unable to use the excess light for photochemistry. Using micro-scale modulated fluorometry, we demonstrated that light scattered by the cystoliths is distributed from the photosynthetically inefficient upper tissue to the efficient, but light deprived, lower tissue. The presence of the cystoliths functioning as light scatterers thus reduces the steep light gradient, enabling the leaf to use the incoming light flux more efficiently for photosynthesis.[3]

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Keywords: *Bioinorganic chemistry; Amorphous materials; X-ray diffraction; Materials science; Photosynthesis;*

Self-assembly, Molecular Recognition and Biomaterials – I

O-109

SELF-ASSEMBLED BIO-INSPIRED NANOSTRUCTURES OF UNIQUE CHEMICAL, PHYSICAL, AND MECHANICAL PROPERTIES

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The significant progress and novel discoveries made in the past two decades in the field of nanoscience and nanotechnology have enabled the fabrication of nano-scale materials and structures with unique and often unprecedented physical and chemical properties. The self-assembly of short peptide building blocks derived from functional biological modules results in the formation of nanostructures of unique chemical and physical properties. By the inspiration from the minimal recognition modules used by nature to mediate coordinated processes of self-assembly, we had developed building blocks that could be directed to form well-ordered nanostructures including nanotubes, nanospheres, nanoplates, and hydrogels with nano-scale order. Based on the molecular architecture of the ultra-rigid aromatic polyamide polymers (such as Kevlar) presenting the aromatic interactions, hydrogen bonds and the stacking of the planar amide bond, these nanostructures represent a new and novel family that is completely different from all other organic nanostructures. These structures also share the heat resistance and chemical stability of the aromatic polyamides. The compact design of the building blocks and therefore their unique structural organization resulted in metallic-like Young‘s modulus of up to 275 GPa, blue luminescence due to high quantum confinement at the nano-scale, and piezoelectric properties comparable to LiNbO3.

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Self-assembly, Molecular Recognition and Biomaterials – I

O-110

DESIGN, PREPARATION, AND STUDY OF STEROID-BASED GELATORS, THEIR GELS AND METALLOGELS

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Supramolecular gels, composed of low-molecular-weight organic compounds, have received a lot of attention over the past two decades[1]. During this time gelation has moved from being a phenomenon observed sporadically in particular molecules, to a controllable and functional process. Supramolecular gels have evolved as a fascinating class of smart and functional nanoscale materials with high potential for a wide range of advanced applications, *e.g.* in sensing, molecular electronics, catalysis, tissue engineering and drug delivery, and as templates for the synthesis of nanoporous materials[2].

The gel formation stems from the spontaneous but controlled self-assembly of low-molecular-weight compounds into fibrous architectures through non-covalent interactions including hydrogen bonding, π-π stacking, electrostatic, and van der Waals interactions, where solvent molecules are entrapped by the entangled three dimensional networks. In the last few years, there has been an increase of interest in the use of coordination chemistry as a rational design route towards self-assembled gel [3]. The binding of a metal ion to a gelator molecule containing an appended ligand site can affect self-aggregation modes and allow the gelation ability to be finely tuned. Although various low-molecular-weight hydro- and organogelators have been reported thus far, examples of gels based on coordination bonds and stimuli- responsive gels generally are still relatively rare. We deal with the design, preparation and study of steroid-based gel [4] responsive to various stimuli (pH, ionic strength, light, redox, *etc.*) and in this work, examples of pH-responsive systems as well as metallogels will be presented.

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Keywords: *Gels; Supramolecular chemistry; Materials science; Steroids; Amino acids;*

Self-assembly, Molecular Recognition and Biomaterials – II

O-111

MACROSCOPIC SELF-ASSEMBLY AND SELF-HEALING THROUGH MOLECULAR RECOGNITION

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In the past three decades much attention has been attracted to molecular recognition and supramolecular complexes. Although there have been numerous attempts on self-organization of molecules, there are a few on self –assembly on macroscopic scale. If molecular recognition works in macroscopic scale, we will be able to realize a variety of architectures and functions. Here we found that macroscopic soft materials can be differentiated each other through molecular recognition. This is the first example of specific molecular recognition events on macroscopic-scale. The concept of supramolecular science will be pushed up as a powerful way on the production of practical materials.

First, a host gel containing β-cyclodextrin(CD) was found to bind a guest gel containing adamantane (Ad) strongly through molecular recognition. In addition, α-CD gel was found to bind the guest gel containing *n*-butyl group specifically and β-CD gel binds that of *t*-butyl groups selectively to give self-assembly on macroscopic scale only by mixing and shaking in water. We used acrylamide gels containing CDs as host gels, and those containing various alkyl groups as guest gels. Each gel was prepared by copolymerization of acrylamide, bis-acrylamide, and acrylamide CD or alkyl acrylates, respectively. Although α-CD gel bound linear alkyl gels, β-CD gel bound cyclic alkyl gels.

We found that a β-CD polymer and a ferrocene-polymer formed a gel. Even when the gel was cut in half, if the gel pieces were brought in contact, the gel pieces were bound and self-healed to the original gel. This gel is redox-responsive.

α-CD gel was found to bind to *trans*-azobenzene gel (Azo-gel). When Azo-gel was irradiated by UV light, the Azo-gel turned to *cis*-azobenzene. Eventually, Azo-gel left α-CD gel and bound to β-CD gel. This is reversible. This is the first discovery that molecular recognition event work in our real world.

Keywords: *Cyclodextrin; Self-assembly; Self-healing; Molecular recognition;*

Self-assembly, Molecular Recognition and Biomaterials – II

O-112

CHARGE-ASSISTED HYDROGEN BONDS AND WEAK INTERMOLECULAR INTERACTIONS AS TOOLS TO FABRICATE COMPLEX SUPRAMOLECULAR ARCHITECTURES

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The rational design of synthetic supramolecular architectures based on well-defined structure-directing forces and hydrogen bonding is still a challenge. We present a supramolecular cage assembled through 72 hydrogen bonds which is constructed from two kinds of hexagonal molecular tiles forming a truncated octahedron, one of the thirteen Archimedean polyhedra (*Science* **2011**, 333, 436). The framework displays an extraordinary ability to encapsulate a wide range of differently charged species, not observed otherwise.

By the exploitation of the same kind of interactions, orientation of polyconjugated guest molecules is obtained in tunable host cavities. The framework host architectures can be controlled systematically in a manner that enables the regulation of the guest orientation and aggregation (*J. Am. Chem. Soc.* **2010,** *132*, 14603). The effects of the distinct packing motifs is manifested as bathochromic shifts in the absorption and emission spectra of the guests as interpreted by ab initio TDDFT calculations.

Interestingly, through CH···pi interactions, the molecular recognition of specific blocks of triblock copolymers by a host molecule promotes the formation of hierarchical periodic structures. The formation of the supramolecular architectures is followed by *in situ*synchrotron X-ray diffraction while the specific CH···pi intermolecular interactions are highlighted by fast-^{1}H MAS NMR and GIAO HF ab initio calculations (*J. Am. Chem. Soc.* **2011**, *133,* 8982).

Moreover, weak intermolecular interactions play a key role in modulating the dynamics of molecular rotors in amphidynamic materials. Indeed, the precise engineering of highly-organized porous silica scaffolds supporting organic elements allows the fabrication of fast molecular rotors ($k > 10^8$ Hz) entirely exposed to the guest molecules which act as regulators (*Angew. Chemie Int. Ed.* **2010**, *49*, 1760).

Keywords: *Crystal Engineering; Block Copolymers; Hydrogen bonds; Materials science;*

Self-assembly, Molecular Recognition and Biomaterials – III

O-113

DNA MATERIALS AND NANOMACHINES

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We build branched DNA species that can be joined using sticky ends to produce N-connected objects and lattices. We have used ligation to construct DNA stick-polyhedra and topological targets, such as Borromean rings. Branched junctions with up to 12 arms have been produced.

Nanorobotics is a key area of application. We have made robust 2-state and 3-state sequence-dependent devices that change states by varied hybridization topology. Bipedal walkers, both clocked and autonomous have been built. We have constructed a molecular assembly line by combining a DNA origami layer with three 2-state devices, so that there are eight different states represented by their arrangements. We have demonstrated that all eight products (including the null product) can be built from this system.

A central goal of DNA nanotechnology is the self-assembly of periodic matter. We have constructed 2-dimensional DNA arrays with designed patterns from many different motifs. We have used DNA scaffolding to organize active DNA components. Active DNA components include DNAzymes and DNA nanomechanical devices; both are active when incorporated in 2D DNA lattices. We have used pairs of 2-state devices to capture a variety of different targets. Multi-tile DNA arrays have been used to organize gold nanoparticles in specific arrangements.

We have self-assembled a 3D crystalline array and have solved its crystal structure to 4 A resolution, using unbiased crystallographic methods. More than ten other crystals have been designed following the same principles of sticky-ended cohesion. We can use crystals with two molecules in the crystallographic repeat to control the color of the crystals. Thus, structural DNA nanotechnology has fulfilled its initial goal of controlling the structure of matter in three dimensions. A new era in nanoscale control awaits us.

Acknowledgement: *This research has been supported by the NIGMS, NSF, ARO, ONR and the W.M. Keck Foundation.*

Keywords: *DNA Nanotechnology; Self-Assembled 3D Crystals; Nanomechanical Devices; N-Connected Objects; Topological Control;*

Self-assembly, Molecular Recognition and Biomaterials – III

O-114

FUNDAMENTAL AND APPLIED ASPECTS OF SOLID ORGANIC INCLUSION COMPOUNDS

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The lecture will highlight some contemporary challenges in understanding properties of molecular solids, and will focus on strategies that may be implemented to tackle these challenges. In many respects, solid host-guest materials based on one-dimensional tunnel host structures (e.g. urea and thiourea inclusion compounds) serve as model systems for exploring and understanding fundamental properties of wider relevance to other classes of materials. Issues of interest include structural properties (including the fundamental understanding of commensurate versus incommensurate behaviour), dynamic properties, host-guest chiral recognition, and order-disorder phase transitions. In addition to these fundamental properties, our recent research has been directed increasingly towards aspects of more direct relevance to potential applications of solid inclusion compounds, including the control of crystal growth processes, studies of guest exchange and guest transport processes, the development of materials for applications as X-ray dichroic filters, and explorations of the related phenomenon of X-ray birefringence. The lecture will present an overview of several inter-related aspects of our research on these materials, as well as highlighting other areas of recent research focused on fundamental aspects of crystallization processes:

(**a**) fundamental and applied aspects of solid inclusion compounds,[1,2]

(**b**) new insights on crystallization processes by confocal Raman microspectrometry,[3]

(**c**) *in-situ* solid-state NMR studies of crystallization from solution.[4,5]

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Keywords: *Solid-state structures; Inclusion compounds; Phase transitions; Crystal growth;*

Self-assembly, Molecular Recognition and Biomaterials – III

O-115

TOWARDS CHARGE STORAGE MEMORY DEVICES BASED ON ELECTROACTIVE ORGANIC MOLECULES

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The increasing interest in miniaturizing electronic devices to achieve denser memories will eventually entail the utilization of molecules as active components. In particular, self-assembled monolayers attached to substrates appear as suitable candidates in*Molecular Electronics* for the development of switchable and memory devices based on electroactive molecules grafted on surfaces.[1] Polychlorinated triphenylmethyl (PTM) radicals are persistent electroactive organic radicals that can be easily reduced to the corresponding anionic species which also show a high stability in solution. Tetrathiafulvalenes are another electroactive species that can be easily oxidized to the corresponding radical-cation and dication states. All such species exhibit different optical and magnetic properties and can be reversibly interconverted in solution by electrochemical techniques.[2] In addition PTM and TTF compounds can be covalently grafted/deposited on surfaces of different nature (Au, SiO_2, HOPG) where they keep their bistability and switchability without degradation.[2]

We will report efforts addressed to functionalize transparent and conducting ITO and Gold surfaces with appropriately functionalized PTM radicals and TTF derivatives. Such hybrid organic/inorganic surfaces behave as chemical and electrochemical redox switches with bistable optical (absorption and fluorescence), magnetic, and wetting responses exhibiting an exceptionally high long-term stability and excellent reversibility and reproducibility.[2] Moreover, such hybrid surfaces can be patterned as well as electrochemically locally addressed enabling to write-store-read information reversibly on the patterned clusters of electroactive molecules. Examples of such nonvolatile molecular memory devices will be presented and discussed.

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Keywords: *Self-assembly; Radicals; Anions;*

Tuesday, 28-Aug 2012

Supramolecular Chemistry and Nanostructured Materials – I

O-244

‘FRUSTRATED’ ORGANIC SOLIDS

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Physical adsorption of gases by a wide variety of materials is an active area of endeavor. Contributions from our group have revolved around solid-solid phase transformations with regard to organic solids. In the process of going from a solvated to a desolvated form of host solid, we have discovered and published on a type of material, which we believe involves a frustration of the solvate lattice as it moves toward the desolvated state. The frustration arises from a reduction in the solvent content within the structure during the desolvation process and results in the formation of a porous material that rapidly sorbs a variety of gases under ambient conditions. In this discussion we further develop applications of frustrated organic solids. Ramifications of early discoveries will also be discussed.

Supramolecular Chemistry and Nanostructured Materials – I

O-245

REACTIVITY IN HALOGEN BONDED CRYSTALLINE MATERIALS

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Discrete and extended cavities are used in many different applications, *e.g.* gas absorption, transport, and conductivity. They can also function as nanoreactors and products formed in such confined environments can differ significantly from those formed in the bulk solution due to the unique constrains the cavity imposes on the reagents.

The dynamic behavior and reactivity in crystalline solids is a field of increasing interest and solid-state reactions induced by external stimuli are useful as they can be employed to synthesize new classes of responsive materials. Recently, we demonstrated that α,ω-bis(trimethilammonium)alkanes diiodides are dynamically porous materials capable of selective uptake of α,ω-diiodoperfluoroalkanes in solution and gas-solid self-assembly processes driven by halogen bonding, the non covalent interaction where halogen atoms work as electron density acceptors.

In this communication we will exploit further the unique and useful opportunities offered by the dynamic behavior of crystalline bis(trimethylammonium)alkane salts. We will describe that the size matching between the cation and self-assembled supramolecular anions allows unstable and previously unknown species to be prepared in quantitative yields. Specifically, we will report that the encapsulating ability of the 1,6-bis(trimethylammonium)hexane cation (hexamethonium cation) and its tendency to pin a tetrahalide dianion $X_2Y_2^{2}$? (X, Y = Cl, Br, I) *via* a net of hydrogen bonds is robust enough to drive the quantitative formation of hexamethonium salts containing the discrete dianions I_4^{2-}, $I_2Br_2^{2-}$, and $I_2Cl_2^{2-}$. These dianions are formed *via* a thermally induced I_2 elimination from hexamethonium salts containing the I_3^-, I_2Br^-, and I_2Cl^- anions respectively. Halogen bonding, hydrogen bonding, and components prearrangement are crucial in allowing for the solid-gas reaction. The reported results prove that the relevance of interactions involving polyhalides can be engineered in the purposeful obtainment of new polyhalides if interactions and their selectivity are maximized in the constrained environment of crystalline solids.

Keywords: *Polyhalides; Self-assembly; Solid-state reactions; Iodine; Gas-phase reactions;*

Supramolecular Chemistry and Nanostructured Materials – I

O-246

SOLUTION-LIKE CHEMISTRY IN CRYSTALS OF NETWORKED MOLECULAR HOSTS

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While many molecular hosts are known to encapsulate specific guest molecules and to induce unusual chemical events in solution, most of them become inactive when they are closely packed in the crystalline state. In porous crystals, however, molecules in fluid pores maintain their solution-like mobility and reactivity. We utilized this pseudo-solution state in porous crystals to transfer solution chemistry into the solid state.

By means of self-assembly strategy, we synthesized porous coordination networks composed of an infinite array of Co_6L_4 (L: 2,4,6-tris(4-pyridyl)triazine) molecular hosts as single crystals. The host subunit was isostructural to a molecular Pd_6L_4 cage which hosts a lot of guests in solution. The crystalline Co_6L_4 host combines molecular-size host cavities and large interstitial pores of 1.2 nm diameter, and solution-like guest accommodation occurs even in a crystalline state. Since guest binding takes place in a single-crystal to single-crystal fashion, the crystal structures of host-guest complexes have been unambiguously determined by X-ray crystallography.

With a pair of solution and crystalline hosts, we can easily transfer unique reactions induced by molecular hosts in solution into a heterogeneous system. When a host-guest complex of Pd_6L_4 cage and 4-hydroxydiphenylamine was treated with EtNCO, chemoselective acylation occurred only on the OH group. The same selectivity was reproduced in the cavity of networked Co_6L_4 cages. Furthermore, this unusual chemoselectivity was explained by crystallographic analysis with crystalline host.

In this presentation, we will present new results of solution-like chemistry observed in crystals of networked molecular hosts.

Keywords: *host-guest systems; X-ray diffraction; Solid-state reactions;*

Supramolecular Chemistry and Nanostructured Materials – II

O-247

PERSPECTIVES IN MOLECULAR TECTONICS

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The design and construction of periodic architectures in the crystalline phase or at surfaces are attracting considerable interest over the last two decades. For both design and analysis of molecular crystals, we have developed a strategy called molecular tectonics which is based on the formation of molecular networks through the design of complementary tectons or molecular construction units. The generation of molecular networks and subsequently of crystals is achieved by self-assembly processes based on repetitive molecular recognition events. This approach, combining supramolecular synthesis and self-assembly processes in the solid state, is operational and versatile and allows the design and construction of a variety of complex purely organic or hybrid architectures. The approach will be presented and illustrated by a variety of tectons and networks.

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Keywords: *Supramolecular Chemistry; Solid-state structures; Crystal engineering; Crystal growth; Cyanides;*

Supramolecular Chemistry and Nanostructured Materials – II

O-248

INTERFACIAL SYSTEMS CHEMISTRY: SURFACE-TEMPLATED ASSEMBLY OF THREE-DIMENSIONAL FUNCTIONAL FRAMEWORKS.

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Supramolecular chemistry holds unique prospects for the fabrication of novel functional materials. Molecularly precisely defined, nanometer-sized subunits which may already be rather complex self-assemble to form even more complex structures which exhibit functionalities not provided by the individual building blocks.

We extend the fabrication of surface-anchored networks beyond the formation of planar, two-dimensional adlayers[1] by demonstrating the synthesis of highly-ordered, three-dimensional porous metal-organic frameworks (MOFs) nucleated on modified Au substrates. We will demonstrate the principle of liquid phase epitaxy[2] for the case of $[Cu_3(BTC)_2(H_2O)_n]$ (HKUST-1) grown on COOH- and OH-terminated SAMs using Cu(II) acetate as the metal precursor and BTC (benztricarboxylic acid) as the organic ligand. The rather different fabrication mechanisms underlying the LPE-process – alternating exposure to the reactants in contrast to the standard solvothermal synthesis – allows to access novel MOF-structures and makes it possible to control the phenomenon of interpenetration.[5]

The availability of porous frameworks rigidly anchored to solid surfaces opens the prospect of adding additional functionality to these ultrathin surface coatings[7] by placing nanoobjects inside the pores within the MOFs, e.g. metal clusters or dye molecules.[6] We will demonstrate the potential of this approach by loading the three-dimensional porous scaffolds with metal-containing molecules such as ferrocene and then characterizing their properties using electrochemistry.

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Keywords: *Metal-Organic Frameworks; Surface Chemistry; Nanotechnology;*

Supramolecular Chemistry and Nanostructured Materials – III

O-249

SUPRAMOLECULAR-TILT-CHIRALITY FOR DESIGNING ORGANIC CRYSTALS AND POLYMERS

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Studies on inclusion compounds of steroids and alkaloids led us to the finding about handedness of two-fold helical assemblies. This finding in supramolecular chirality has been connected with the following two facts. First, the handedness lie in seventy percent of over 600,000 crystal data according to the Cambridge Structural Database. Second, one can catch the handedness in the form of two-fold helical molecular assemblies, bundles of the helical assemblies, as well as complimentary helical assemblies of host and guest components.

This presentation deals with discrimination of right- or left-handedness in supramolecular-tilt-chirality on the basis of two- or multi-point approximation method. The discrimination in supramolecular-tilt-chirality for organic crystals has consistency with that of molecular chirality for chiral molecules and helical polymers. The conventional crystallographic theory is surely correct in the case of atoms and ions with spherical symmetry, but is not always correct in the case of organic molecules with various shapes.

The supramolecular-tilt-chirality method is effective for designing organic crystals and polymers with two-fold helices. We applied this to bundling of two-fold helical hydrogen-bonded networks as well as so-called asymmetric crystallization of achiral organic molecules, such as polyaromatic compounds. We now know that most of organic crystals consist of helical assemblies with right- or left-handedness, likewise biopolymers such as DNA and proteins.

A series of aliphatic ammonium anthracenedisulfonates have enabled us to diversely arrange their anthracene moieties in the crystalline state. These moieties allowed us to observe static and dynamic modulations of optical and electrical properties. The systematic investigation indicates a relationship between the arrangements and the properties. Finally, this presentation covers a hierarchical construction of inclusion crystals consisting of 1,8-anthracenedisulfonate and triphenylmethylamine through chairlike hydrogen bonding networks. Such crystals have stacked ellipsoidal supramolecular beads which exhibit guest-responsive fluorescence.

Keywords: *solid-state structures; helical structures; chirality; fluorescence; supramolecular chemistry;*

Supramolecular Chemistry and Nanostructured Materials – III

O-250

MESOPOROUS AND MICROPOROUS MATERIALS FOR BIOMEDICAL APPLICATIONS

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Porous materials such as zeolites L, and ordered mesoporous silica systems are interesting containers which can reach small dimensions and can with appropriate functionalization be biocompatible. In this talk I will show that silica based materials can be used to target label and kill antibiotic resistant bacteria using light. The multifunctional nanocontainers can be used for diagnostics purposes and their uptake by different type of cell will be shown. The combination of imaging and deliver will be demonstrated with a very recent result. Cellular uptake of nano-size zeolites can be followed by fluorescence microscopy and molecules entrapped inside the channels of the zeolites can be delivered into the nucleus of the cells. Indeed the channels can be opened upon degradation of a polymer used to coat the entire crystals.

Finally the use of these silica materials for the patterning of surfaces will be discussed. The pattern can be obtains using micro contact printing and the functionalization with biomolecules will lead to the cell adhesion only in desired patterns. The use of chiral systems will allows the immobilization of only desired type of cells.

Supramolecular Chemistry and Nanostructured Materials – III

O-251

CHEMICAL REACTIONS OF MOLECULAR CRYSTALS AND AGGREGATES UNDER HIGH PRESSURES

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In the last years information on chemical reactions at high pressures in molecular crystals and other molecular aggregates has been growing steadily involving a variety of systems and among others simple second row diatomics and triatomics, hydrocarbons, energetic materials, alcohols, clathrate hydrates. With the available data it is feasible to attempt a classification of high pressure chemical reactions primarily into reversible and irreversible processes depending of the free energy profile from reactants to products and its modification going from ambient to high pressures and the heigth of the enrgy barriers. In several experiments and in *ab initio* molecular dynamics modeling the role of excited electronic states in high pressure reactivity has been highlighted and a novel dynamic view of the topochemical principle has been brougth forward as a source of selectivity in high pressure processes as a subsection of solid state chemistry. The collective character of high pressure solid state reactions has also been evidenced. The synergy of the combined use of pressurization and photoactivation has been shown to be an invaluable source of information on the the high pressure reaction mechanisms.

These concepts will be discussed with results on high pressure reactions in simple hydrocarbons (condensation, polymerization, amorphization), on simple alcohols and on clathrate hydrates.

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Keywords: *high pressure chemistry; solid state chemistry; photoactivation;*

Nanoporous Materials – I

O-404

CONTROLLING AND MAINTAINING THE STRUCTURE OF TEMPLATED POROUS MATERIALS

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Nanoporous and nanostructured materials are becoming increasingly important for advanced applications involving, for example, bioactive materials, catalytic materials, energy storage and conversion materials, photonic crystals, membranes, and more. Templating methods based on hard templates (colloidal crystal templating, nanocasting) and soft templates (surfactant systems) provide access to nanostructured porous materials in which both the internal pore architecture and the material's morphology can be controlled at a range of length scales from the subnanometer to the millimeter scale. Significant benefits of materials with structural features of nanometer and submicrometer dimensions have been demonstrated for numerous applications, at least at the proof-of-concept stage. Some applications profit from short diffusion paths in hierarchical nanostructures. Other applications take advantage of the relatively high surface areas of nanoporous solids and the often associated improved reactivity. However, in many applications the operating environment puts extreme demands on the material, perhaps due to external and internal mechanical forces, high temperatures needed for efficient operation, or involvement of the material in a reaction. It can be difficult to maintain structural features at small length scales and even bulk morphologies under those conditions. This presentation highlights methods of controlling pore architecture and materials morphology and will then outline limitations and recent advances in stabilizing porous materials under reactive or high temperature conditions.

Keywords: *Template synthesis; Mesoporous materials;*

Nanoporous Materials – I

O-405

SILICA MESOPOROUS CRYSTALS WITH ICOSAHEDRAL AND DODECAGONAL-PRISM MORPHOLOGIES; MULTIPLY TWINNED OR QUASICRYSTALLINE?

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A mesoporous silica crystal is formed through co-operative self-organisation of surfactant and silica in water. We have confirmed by electron crystallography that sphere packing (Space groups (SGs): Fm-3m, $P6_3mmc$), polyhedra packing (SGs:Fd-3m,Pm-3n, $Cmmm$, $P4_2/mnm$), cylindrical (SG:$p6mm$) and bi-continuous (SGs: Ia-3d, Pn-3m) structures are formed in this order as surfactant concentration increases. Most of mesoporous silica crystals show characteristic morphology which is commensurate with crystallographic point group symmetries.

We have synthesized a crystal which shows well-resolved powder XRD profile but its icosahedral morphology does not fit any crystallographic point group symmetry in the sphere-packing regime.[1] Furthermore, recently we have succeeded in synthesising a mesoporous silica crystal, which indicates twelve-fold symmetry in both morphology and electron diffraction pattern in polyhedra-packing regime.[2]

From electron microscopy (EM), the crystal with icosahedral morphology is multiply-twined particle (MTP) of FCC structure and the second one is a dodecagonal quasicrystal in the center surrounded by twelve fans of crystalline domains in the peripheral part.The details will be given at the Conference.

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Nanoporous Materials – I

O-406

IONOSILICAS: PERIODIC MESOPOROUS ORGANOSILICAS FROM IONIC PRECURSORS

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Ionosilicates (or so-called ‘i-silicas’) are defined as silica based materials containing covalently tethered ionic groups. These materials, situated at the interface of silica hybrid materials and ionic liquids, have large potential in catalysis, molecular recognition and separation. This talk will summarize our ongoing efforts in different areas related to the synthesis and applications of i-silicas. In a first part, we will focus on different aspects of the formation of i-silica phases displaying defined architectures on a mesoscopic level. I-Silicas are obtained *via* template directed hydrolysis-polycondensation reactions using ionic trialkoxysilylated precursors. Nanostructured phases can be obtained thank to specific interactions of these ionic precursors with complementary surfactants. We will show that the formation of structured phases can be achieved from suitable surfactant-precursor ion pairs. This approach is particularly appealing as both the nature of the organo-ionic part of the precursor and the the chemical constitution of the surfactant can be modulated. The second part is devoted to applications of i-silicas in catalysis and separation. I-Silicas show interesting catalytic properties in various organocatalytic reactions. In several cases, synergistic effects between silica support and the tethered ionic substructure allow increasing significantly the catalytic activity compared to pure ionic liquids. Finally, i-silicas appear as efficient ion exchange materials displaying Hofmeister selectivity.

Keywords: *Periodic mesoporous organosilica; Ionic liquids; Template syntheses;*

Nanoporous Materials – II

O-407

NANOPOROUS ORGANIC-INORGANIC HYBRID MATERIALS: POROSITY MEETS SURFACE CHEMISTRY

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Nanoporous organic-inorganic hybrid materials with ordered pore structures exhibit a high potential for important applications like gas storage and separation, heterogenous catalysis, sensors and drug release. The usage of appropriate organic-inorganic precursors in the presence of structure-directing agents allows the synthesis of micro- or mesoporous hybrid materials with defined high porosity and tailored surface chemistry. This lecture is dealing with the principles of the synthesis strategy of microporous metal-organic frameworks (MOFs) and periodic mesoporous organosilicas (PMOs) as well as with the application of these materials for storage, separation and light harvesting.

Keywords: *Metal-organic Frameworks; Mesoporous materials;*

Nanoporous Materials – II

O-408

POROUS ORGANIC MATERIALS

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Porous organic materials such as *__H__yper-__C__ross-linked __P__olymers* (HPCs) and *__P__olymeric __P__orous __N__etworks* (PPNs) have raised considerable interest in the material science community due to their host-guest interactions. The pores within these materials are indeed capable of specific host uptake and release. This opens the door to applications such as gas storage and separation but also to racemic resolution and asymmetric synthesis if materials bearing enantiomerically pure pores are used.

In contrast to inorganic material such as zeolites or hybrid networks like *__M__etal __O__rganic __F__rameworks* (MOFs), purely organic porous materials convince by unreached low densities which are particularly appealing for the automotive sector and by their ease of processing, post-functionalization and of introducing chirality.

We have developed an easy and rapid access to *__t__etra__p__henyl__m__ethane* (TPM) and *__t__etra__p__henyl__a__damantane* (TPA) as well as to *__h__exa__p__henyl-p-__x__ylene* (HPX) cores. These tetrahedral and pseudo-octahedral molecules serve as precursors out of which a whole range of different tectons can readily be prepared and serve directly for network generation.

Using the same concept of modularity, we also prepared some fullerene hexakis adducts bearing octahedral topology. These tectons will again serve for networks generation.

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Keywords: *Organic Materials; Click chemistry; Porous networks; Gas storage;*

Nanoporous Materials – III

O-409

POROUS AROMATIC FRAMEWORKS: SYNTHESIS, STRUCTURE, AND FUNCTIONS

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In last decades, many efforts were applied to improve the surface area and heat of adsorption of artificial porous materials. Among those synthesized ultrahigh surface area porous solids, porous aromatic frameworks (PAFs) express highest Brunauer-Emmett-Teller (BET) surface area and excellent physicochemical stability to meet the criteria of post-combustion. In 2009, our group have developed a method to synthesis the first long range ordered PAFs with dia topology (PAF-1), which show a record surface area ($S_{BET}=5640$ m^2 g^{-1}) at that time and exceptional physicochemical stability via a nickel(0)-catalyzed Yamamoto-type Ullmann cross-coupling. Besides, PAF-1 also shows very high uptakes of carbon dioxide (1.3 g g^{-1} at 40 bar, 298 K) to make it a good candidate for carbon dioxide storage. Recently, this record was broken by a porous aromatic polymer network PPN-4, which shows the BET surface area as high as 6461 m^2 g^{-1}. Combined with such an impressive surface area, PPN-4 can adsorb 2121 mg g^{-1}CO_2 (212 wt %) at 50 bar and 295K. Before PPN-4 was reported, same porous organic framework had already been synthesized by Cooper's group ($S_{BET}=1102$ m^2 g^{-1}) and our group as PAF-3 ($S_{BET}=2932$ m^2 g^{-1}) independently via Yamamoto type Ullmann cross-coupling with different synthesis conditions. In addition to the dramatic CO_2 storage properties of PAFs, we also find that PAFs have high selective adsorption properties on green house gas such as CO_2 and CH_4. Zhou also report high selectivity of CO_2/N_2 by grafting sulfonic acid and its lithium salt on the framework of PAF-1. These progresses indicated that PAFs is such a robust material that not only store large amount CO_2 at high pressure but also selectively adsorb green house at ambient condition which meet the criteria of post-combustion capture of CO_2.

Keywords: *Adsorption; Microporous materials; Host-guest systems; Carbon dioxide fixation; Molecular recognition;*

Nanoporous Materials – III

O-410

METAL ORGANIC FRAMEWORKS FOR CLEAN ENERGY APPLICATIONS

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Until affordable green options are available, fossil fuels will remain a primary source of energy. Carbon capture represents a means of mitigating the greenhouse effects of fossil fuel combustion. This approach also presently carries significant costs making widespread adoption challenging. Part of this presentation will focus on the opportunities and challenges to make fossil fuel energy production greener including the idea of solid sorbents, such as metal organic frameworks (MOFs), for gases.

MOFs represent tunable molecular scaffolding that can be adjusted for a breadth of applications. This presentation will concern our efforts towards tailoring the properties of MOFs towards energy challenges.[1] The first concerns our efforts to make MOFs with amine lined pores for CO_2 capture. In contrast to liquid amines which chemisorb CO_2 and have high energy costs for regeneration, the MOF approach gives physisorbed gases and hence more facile release. Despite the weaker binding mode, we will show that high selectivities are possible owing to heats of adsorption over 40 kJ/mol.[2] A key challenge for this field is to make MOFs that are more hydrolytically stable. Some of our recent results concern efforts to make more water stable MOFs using phosphonates and related linkers.[3]

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Keywords: *MOFs; CO_2 capture; Porous solids;*

Nanoporous Materials – III

O-411

LUMINESCENT MOLECULES CONFINED IN POROUS AND LAYERED MATERIALS: ENHANCED PHOTOEMISSION PROPERTIES AND OPTOELECTRONIC APPLICATIONS

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The confinement of luminescent dyes and polymers into the nanospaces of porous or layered materials may prevent molecules aggregation and improve their thermal and photochemical stability along with their photoemission properties. These requirements are key points for the development of efficient hybrid optoelectronic devices (HLED). In this field, our research group recently developed novel hybrid luminescent solids based on nano-sized MCM-41 and platelet SBA-15 silica containing inside the pores fluorescein and electroluminescent polyphenylenevinylene (PPV) co-polymer (super yellow), respectively.[1] Higher quantum efficiency, mainly related to a reduction of aggregates of the pure dyes, and improved photostability were observed in both host-guest systems. Moreover, hybrid photonic antenna based on SBA-15 solid, where an encapsulated donor (PPV co-polymer) transfers the photoexcitation energy directly to an acceptor (cyanine dye) covalently linked on the external surface was also developed as promising candidate for use in optoelectronic devices.

Recently, luminescent organo-modified layered materials were syntesized and tested as light-emitting film in HLED devices. The structural properties along with their tunable hydrophilicity/hydrophobicity render these solids suitable to host and stabilize different luminescent entities. In this respect, two systemes will be described: **i**) a synthetic saponite intercalated with a luminescent polyhedral oligomeric silsesquioxane (POSS) bearing in the structure a cyanine molecule and **ii**) a hydrotalcite decorated on the surface with electroluminescent semiconductor quantum dot crystals.[2] Both systemes were used as emitting films in LED devices, because of their enhanced quantum yield efficiency and improved photostability.

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Novel Materials and Molecular Interactions

O-412

POROUS AMORPHOUS ORGANIC CAGES: AN EXPERIMENTAL AND MOLECULAR DYNAMIC SIMULATION STUDY.

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The design of porous organic molecular solids where packing is dictated by weak van der Waals forces is attracting considerable attention. We have developed a series of organic cage molecules that can be used for the construction of self-assembled crystalline porous materials. Furthermore, we have found these cage molecules can badly pack, creating permanent porosity in the amorphous solid state. Interestingly, the gas selectivity in these amorphous cage materials can be fine tuned by varying the ratio of reagents in the reaction. A better understanding of this phenomenon will aid in the optimization and development of industrial applications of these amorphous materials in separation and catalytic process.

An alternative approach for characterizing these amorphous materials is based on molecular simulations. We developed a methodology to generate simulated structures of amorphous cage materials. All simulated models are characterized by their porosity with surface area, pore size distribution, density and microporous volume. The results show good agreement with available experimental data. The dynamic diffusion of gas molecules (mainly H_2, N_2) through cavities or pores of amorphous organic cages were investigated using MD simulations. The trajectory of H_2 in amorphous cage **1** exhibits a broader range of displacement compared to N_2, which indicates a faster diffusion of H_2. Therefore, amorphous cage **1** displays gas selectivity for H_2 over N_2. We also suggest that the enhanced porosity in these amorphous solids results predominantly from the extrinsic porosity.

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Keywords: *Molecular dynamics; Micropore materails; Cage compounds; Nanostructures;*

Novel Materials and Molecular Interactions

O-413

AMINOGUANIDINE AND DIAMINOGUANIDINE AS ADAPTIVE CATIONIC BUILDING BLOCKS IN ORGANOSULFONATE STRUCTURES

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Crystal engineering is a very delicate process which depends on many factors, and, as a consequence the final structure can rarely be predicted. Crystal engineering usually overcomes these obstacles by relying on strong, directional interactions like hydrogen bonding and dipolar forces.

The structural backbone of one of the most versatile and widely used systems, guanidinium-sulfonate assemblies, is a honeycomb lattice of $R^2_2(8)$ H-bond rings which assemble into ribbons and larger $R^3_6(12)$ patterns. The numerous papers published on this subject provide ample amounts of data on the effect of organic R substituent on crystal packing and overall structure type (bilayer, brick etc.).

To our knowledge no attempt was made to change the cationic component in these systems, the guanidinium moiety. The aim of the current work is to investigate the structural versatility of aminoguanidine and diaminoguanidine as cationic components together with representative organic sulfonates.

The 7 new crystal structures demonstrate the versatility of these new cationic components to form supramolecular hydrogen-bonding assemblies. Furthermore, aminoguanidine proved to be adaptable, by forming a $R^2_2(10)$ dimer in the structures where the total number of hydrogens available of H-bonding exceeds the total number of H-bond acceptors. Diaminoguanidine presented this motif in all the structures studied, with the orientation of the elongated dimer mimicking the width of the organic group from the sulfonates.

Keywords: *crystal engineering; hydrogen-bond patterns;*

Novel Materials and Molecular Interactions

O-414

MATRIX-ISOLATION AND AB INITIO STUDY OF THE COMPLEX BETWEEN FORMIC ACID AND XENON

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Formic acid (HCOOH, FA) is a useful model compound for understanding the properties of more complicated molecules and the intermolecular interactions, in particular, of biological interest. As the simplest organic acid, FA exhibits the conformational isomerism with respect to the rotation about the single C-O bond, which is a typical phenomenon in the conformational processes in carboxylic acids. Light-induced conformational change has allowed preparing dimers and complexes of the higher-energy conformer. Since rare-gas matrices are widely used to study conformational changes, understanding of the interactions between rare-gas atoms and different conformers is important. In present work, we study the complexes of *trans*- and *cis*-FA with a Xe atom using IR spectroscopy in an argon matrix. The geometries, interaction energies, reaction barriers, and vibrational spectra of the 1:1 FA···Xe complexes are calculated by the *ab initio* method at the MP2 level of theory. The calculations reveal four structures for the *trans*-FA···Xe complex and four structures for the *cis*-FA···Xe complex. In the experiments, two structures of the *trans*-FA···Xe complex are observed after deposition of FA/Xe/Ar matrices, with and without OH···Xe interaction (H-bonded and non-H-bonded structures). The *cis*-FA···Xe complex was synthesized by vibrational excitation of the non-H-bonded *trans*-FA···Xe complex. The non-H-bonded and H-bonded structures of the *cis*-FA···Xe complex are observed after the excitation. The decay of the H-bonded and non-H-bonded *cis*-FA···Xe complexes in an argon matrix is, respectively, substantially slower and faster compared to the *cis*-FA monomer. This observation is explained by the different tunnelling barriers for these species. This is the first experimental report of the non-H-bonded complex for *cis*-FA. This work is partially motivated by anaesthetic properties of xenon, which enhances the importance of research on the interaction between Xe atoms and organic molecules.

Keywords: *Ab initio; formic acid; xenon; Tunnelling; Matrix isolation;*

Novel Materials and Molecular Interactions

O-415

IONIC NANOPARTICLE NETWORKS: NEW VERSATILE HYBRID MATERIALS

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Recently ionic nanoparticle networks (INN) were reported in the frame of the remarkable development of new inorganic-organic hybrid materials based on nanoparticle assembly. The original method we developed to synthesize 3-D networks is based on the functionalization of metal oxide nanoparticles with ionic linkers, the bridging ligands containing imidazolium units. Recent publications pointed out the powerful synergy of ionic species with nanoparticles. Such synergy makes those new inorganic-organic hybrid materials promising candidates for many applications such as catalysis or luminescent devices, as will be exemplified in this communication.

Focusing on catalysis for CO_2 activation reactions, the combination of high imidazolium content with the presence of metal centers, also able to coordinate to CO_2 molecules, makes the hybrid materials INN highly promising catalysts. In addition the imidazolium bridging units in the final hybrid material renders the INN tailorable, while the INN materials are solid, which allows an easy separation of the catalyst after reaction. Thus, INN materials, with mono- and di-imidazolium bridging units as well as with various counter anions, were investigated as catalysts for the cycloaddition of CO_2 into different starting epoxides.

The photoluminescent properties of INN were also studied. It appears that INN materials are luminescent in the visible range. The excitation wavelength as well as the wavelength of maximum emission can be tailored when modifying the imidazolium linker used to link the nanoparticles. In parallel, the short-range order of the network was investigated via small-angle X-ray scattering. This short-range order was interpreted as originating from self-organization of the aromatic rings of the ligands bridging the nanoparticles by means of pi-pi stacking. This hypothesis was validated by luminescence investigations on the hybrid materials.

Keywords: *Materials Science; Nanoparticles; Luminescence; Stacking interactions; Cycloaddition;*

Novel Materials and Molecular Interactions

O-416

A NEW MONAZITE PHASE FORMED FROM STRONTIUM FLUOROPHOSPHATE

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Fluorophosphates (PO_3F^{2-}) are a fluorine derivative to an orthophosphate (PO_4^{3-}), with the tetrahedral unit possessing at least one P-F bond. Although these materials have been known since the early 1920's, with a number of uses, particularly in dental care, their exploitation as a structural building block to new materials has been limited. To date, fewer than 25 structurally characterized monofluorophosphates have been reported.

Our research has initially focused on the substitutional chemistry possible when PO_4^{3-} is replaced by PO_3F^{2-}. To this end, we report the novel synthesis of a monazite structured $SrPO_3F$, formed from a readily available PO_3F^{2-} precursor via a precipitation reaction.

Detailed structural studies, performed using neutron powder diffraction, X-ray fluorescence and Raman spectroscopy confirm $SrPO_3F$ adopts the important monazite structure type (MXO_4), which is more commonly associated with rare earth phosphates such as $LaPO_4$[1]. This compound crystallises with space group ($P2_1/n$) and unit cell parameters $a = 6.97293(6)$?, $b = 7.11850(5)$?, $c = 6.71991(5)$? and $\beta = 101.7629(7)°$. The structure consists of distorted PO_3F^{2-} tetrahedron which form chains both parallel and perpendicular to the *a* axis, with an apparent ordering of the P-F bond and consequently the orientations of the distorted PO_3F^{2-} tetrahedra. This study also investigates the stability of these new materials.

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Keywords: *Materials Science;*

Novel Materials and Molecular Interactions

O-417

HIGHLY POROUS CARBON MATERIALS FROM DICYCLOPENTADIENE HIGH INTERNAL PHASE EMULSIONS (HIPES)

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The present work relates to the preparation of a three-dimensional carbonaceous polyHIPE material using a high internal phase emulsion (HIPE) templating technology. Porous carbonaceous materials represent outstanding candidates for a range of applications such as water and air purification, adsorption, catalysis, electrodes and energy storage materials[1]. Using high internal phase emulsion (HIPE) templating technology[2], porous carbonaceous materials can be obtained after the carbonization and the pyrolysis with fully accessible network, high (macro)pore volume of up to 10 cm^3/g and in a different shapes.

Carbon precursor used in present work is an economically interesting monomer while it is a by-product of steam cracking of naphta and gas oils namely dicyclopentadiene (DCPD) which is cheap and readily available. PolyDCPD HIPEs posses very favourable mechanical properties.[3] After the pyrolysis material undergoes major dimensional shrinkage (by factor of 2) however, interconnected porous morphology is completely maintained whit additional microporosity in the polymer walls.

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Keywords: *microporous carbon polymers; ring opening metathesis polymerization;*

Molecular and Hybrid Porous Crystals

O-513

PERMANENT POROUS MATERIALS FROM SHAPE-PERSISTENT ORGANIC MOLECULES

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Porous materials derived from discrete organic compounds became a real alternative to systems like zeolites, metal-organic frameworks, covalent organic frameworks or amorphous porous organic polymers.

The rational construction of molecular organic precursors, their synthesis and formation of functional porous materials are discussed. The compounds form porous materials with very high specific surface areas for both types of materials, intrinsic and extrinsic, achieving values of up to 2796 m^2g^{-1}.[1–3] Furthermore, the processing porous molecules into functional devices is presented.

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Keywords: *Crystal engineering; Materials science; Schiff bases;*

Molecular and Hybrid Porous Crystals

O-514

GAS STORAGE AND SELECTIVITY IN POROUS METAL ORGANIC FRAMEWORK MATERIALS

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Metal-organic framework (MOF) complexes, constructed via combination of metal nodes with designed polychelate bridging ligands, are important hybrid materials that can show permanent porosity and excellent gas storage capabilities. Understanding the molecular mechanisms by which these porous materials trap gases is essential for the design of improved systems. In this lecture we focus on MOFs for the selective capture of CO_2 from flue gases, and describe the synthesis, properties and structures of a series of new porous materials derived from Al(III) and In(III) with isophthalate carboxylate bridging ligands showing novel structures and pore decoration.

Materials functionalised with amine-groups dominate the area of CO_2 capture largely because of their potential to form carbamates *via* $H_2N(\delta-)$—$C(\delta+)O_2$ interactions, thus trapping CO_2 covalently. We report the synthesis and structure of a unique non-amine-containing porous solid NOTT-300 in which hydroxyl groups within the pores bind selectively to CO_2. NOTT-300 exhibits highly selective uptake of CO_2 versus N_2, CH_4, H_2, CO, O_2, Ar, and *in situ* powder X-ray diffraction (PXRD) and inelastic neutron scattering (INS) studies, combined with density functional theory (DFT) modelling, reveal that these hydroxyl groups bind CO_2 *via* the formation of $O=C=O(\delta-)\cdots H(\delta+)$—O hydrogen bonds. These are reinforced further by weak supramolecular interactions with C-H hydrogen atoms on the phenyl rings. This offers exciting potential for the application of new capture systems based on the soft binding of CO_2 via the use of an 'easy-on' and 'easy-off' model. Parallel studies using PXRD, INS and DTF on the capture of SO_2 have defined the structure of SO_2-loaded NOTT-300. Furthermore, with In(III) we report an unprecedented partially-interpenetrated network showing high selectivity for CO_2 based upon a defect structure that can be modelled by grand canonical Monte Carlo simulations.

Keywords: *metal organic framework materials; gas storage; inelastic neutron scattering; powder x-ray diffraction; CO2 and SO2;*

Molecular and Hybrid Porous Crystals

O-515

MODELLING COMPLEX STRUCTURE, POROSITY, AND CO-OPERATIVE DIFFUSION BEHAVIOUR IN MOLECULAR POROUS ORGANIC MATERIALS

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Materials with molecular-scale porosity are important in a wide range of applications such as gas storage, molecular separation, and heterogeneous catalysis. Understanding complex gas sorption behaviour can give important information about the structural properties of a material and gas uptake mechanisms.[1, 2] We are developing novel methodologies for investigating the structure, time-dependent pore connectivity, co-operative diffusion mechanisms, and stepped gas sorption uptake behaviour.

Discrete molecules tend to pack efficiently in the solid state resulting in minimal void volume, hence very few molecular materials exhibit permanent porosity. Molecular porous materials are able to respond locally to the presence of a guest leading to the potential for diffusion of molecules that would not be expected by analysis of the static crystalline structure.

Here, we analyse molecular porous solids, for example Cage **3** that packs to form a diamondoid 3-D pore structure running through restrictive cage windows.[3, 4] We show that by analysing the dynamic surface area properties of the molecular material as guest molecules diffuse, we can identify and understand the co-operative diffusion mechanisms. This will allow us to potentially design materials with porosity tailored for a specific application.

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Keywords: *Microporous materials; Molecular dynamics; Surface analysis; Solid state structures;*

Hybrid Zeolites and Nanochemistry

O-516

ENI CARBON SILICATES: TRULY HYBRID ORGANIC-INORGANIC ZEOLITES

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ECS materials form a new class of porous crystalline organic-inorganic hybrid aluminosilicates recently discovered, whose synthesis resembles that of zeolites, involving the hydrothermal treatment of a reaction mixture composed by $NaAlO_2$ and a bridged silsesquioxanes $[(R'O)_3Si{-}R{-}Si(OR')_3$, $R = $ alkyl or aromatic groups; $R' = Me$ or $Et]$ as sources of alumina and silica, respectively. A set of ECS materials has been synthesized so far, by varying the nature of the bridged silsesquioxanes and the synthesis conditions. The characterization of these materials demonstrated that most part of the silica precursor does not undergo Si-C hydrolysis and are present unchanged in the crystalline phases. Though challenging because of the complexity of the XRD patterns, the determination of the crystal structure of some ECS materials was successful, providing important information on their characteristics. The ECS structures known so far consist of a stacking of alternating inorganic and organic layers and possess microporous systems, whose architecture varies from a phase to another. Taking into account the materials obtained with R = phenylene, different situations exist. ECS-2 is a clathrasil-like structure since the arrangement of the phenylene rings in the organic layers produces large cages not open to the exterior. In the structure of ECS-3 the relative arrangement of the phenylene rings generates an open porosity running within the organic layer only. More interesting is ECS-14 because it represents the first example of hybrid material with the structure related to a known zeolite framework type, i.e. AFI common to AlPO-5 and the silica SSZ-25 phases. The 12-membered ring linear channels are present even in ECS-14, crossing the inorganic and organic layers which stack along [001]. For other ECS materials, the structure determination is in progress and the results will be illustrated and discussed to provide an overview of this interesting class of materials.

Keywords: *Zeolites; Microporous materials; Layered compounds; X-ray diffraction; Electron diffraction;*

Hybrid Zeolites and Nanochemistry

O-517

HIGH PRESSURE WATER INTRUSION INVESTIGATION ON PURE SILICA CAGE-LIKE STT-TYPE ZEOLITE: INFLUENCE OF THE MINERALIZING AGENT

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Crystalline pure silica polymorphs of microporous nature are attractive materials for several applications, especially in the energetic field. In these hydrophobic materials, the adsorption of water is extremely weak when the pressure is below the water saturation vapor pressure. By submitting these porous solids (zeosils) to an increasing hydrostatic pressure, the intrusion of water into the microporous matrices is observed. Depending on various physical parameters related to the porous material, the "zeosil-water" system is able to restore, dissipate or absorb the supplied mechanical energy during the compression step and therefore displays a spring, shock-absorber or bumper behavior. Cage-like system as STT-type zeosils has been studied and their experimental water intrusion–extrusion isotherms were performed at room temperature. These "zeosil–water" systems behave like a molecular spring and the phenomenon is reproducible over several cycles. The samples were obtained using two synthesis routes: hydroxide (SSZ-23(OH)) and fluoride media (SSZ-23(F)). Different characterizations have been realized before and after water intrusion–extrusion experiments in order to reveal the presence or not of defects after such experiments. For all samples, no structural modifications at the long range order were observed by XRD analysis. ^{29}Si solid state NMR spectroscopy confirmed the presence of a small amount of silanol defects in the calcined materials which is more pronounced for the SSZ-23(OH) sample. Nevertheless, the amount of silanol defects observed is quite low (< 3% for SSZ- 23(F) and < 6% for SSZ-23(OH)). After intrusion-extrusion of water, due to the breaking of some siloxane bonds, the number of defect sites increases and consequently part of water still remains in the structure. However, for both SSZ-23 samples the "STT zeosil-water" can restore more than 80 % of the stored energy corresponding to about 7.0 J.g^{-1}.

Keywords: *Hydrophobic zeolite; STT-type zeolite; water intrusion-extrusion experiments;*

Hybrid Zeolites and Nanochemistry

O-518

SURFACE MODIFICATION OF ITO LAYERS BY AFM-BASED ELECTROOXIDATIVE LITHOGRAPHY

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Transparent conductive oxides like indium tin oxide (ITO) are fundamental components in manifold technological applications. The modulation of ITO surface properties, such as wettability, adhesion, and conductivity, is crucial to its integration in complex frameworks. Silane-based self-assembled monolayers (SAMs) have proved reliable systems to tailor the oxide surface properties.[1] The site-selective oxidation of SAMs by electro-oxidative probe lithography enables the assembly of nanoscale structures by supramolecular chemistry.[2]

Here, we report for the first time the nanoscale oxidation of octadecyltrichlorosilane (OTS) monolayers onto ITO films by electro-oxidative probe lithography. The lithographic process results in a local overoxidation of the substrate, as confirmed by tests onto bare ITO. Moreover, the monolayer oxidation causes the conversion of $-CH_3$ groups into hydrophilic functionalities. This phenomenon was exploited to further modify the surface by site-selective growth of Ag nanoparticles. The oxidation process was studied by Scanning Kelvin Probe Microscopy (SKPM) and compared to the oxidation of the non-coated oxide and of the "reference" OTS-Si. Marked difference related to the oxidized monolayer are appreciable in SKPM images, which are not observable in topography or lateral force images. SKPM thus represents a powerful tool to investigate the monolayer oxidation.

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Keywords: *ITO; octadecyltrichlorosilane; electro-oxidative lithography; scanning Kelvin probe microscopy; atomic force microscopy;*

Solid State Chemistry and Nanochemistry

O-519

METAL-ASSISTED GROWTH OF GERMANIUM NANOWIRES: OPPORTUNITIES USING SOLID METAL SEEDS

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One-dimensional (1D) semiconductor nano-architectures with tunable morphologies, dimensions, crystallographic phases and orientation are of tremendous interest for a broad range of applications.[1] Metal-seeded growth of 1D semiconductor nanostructures is still a very active field of research, despite the huge progress which has been made in understanding this fundamental phenomenon. Liquid growth promoters allow control of the aspect ratio, diameter and structure of 1D crystals via external parameters, such as precursor feedstock, temperature and operating pressure. However the transfer of crystallographic information from a nanoparticle seed to a growing nanowire has not been described in the literature. We investigated the formation of Ge nanowires using solid metal growth promoters in a process based on thermal decomposition of diphenylgermane. The theoretical requirements for transferring information such as defects from nanoparticle seeds to growing semiconductor nanowires have been defined and we describe why specific metal nanoparticles are ideal candidates for this purpose.[2] Significantly, under certain reaction conditions {111} stacking faults in the noble metal seeds can be directly transferred to a high percentage of <112>-oriented Ge nanowires, in the form of radial twins in the semiconductor crystals. In addition, we will detail the influence of solid growth seeds on the crystal quality of Ge nanowires and demonstrate size-selective growth in the sub-20 nm diameter regime.[3] Controlled defect transfer from nanoparticles to nanowires could open up the possibility of engineering 1D nanostructures with new and tuneable physical properties and morphologies.

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Keywords: *Crystal growth; Chemical vapor deposition; Nanostructures; Electron diffraction;*

Solid State Chemistry and Nanochemistry

O-520

STRUCTURAL CHARACTERIZATION AND TRANSPORT PROPERTIES OF CVT GROWN ZRSE3 AND ZRS3 CRYSTALS.

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Single crystals of $ZrSe_3$ and ZrS_3 are family of materials with low symmetry structure were grown by chemical vapour transport technique using iodine as a transporting agent. The grown crystals were characterized by energy dispersive analysis of X-ray (EDAX) for confirmation of stochiometric proportion of constituent elements and structure of grown crystals was determined by X-ray diffraction (XRD) technique. The resistivity and thermoelectric power measurements were carried out in the temperature range 308 K to 573 K. The Hall coefficient, carrier concentration and Hall mobility were determined from Hall Effect measurements at room temperature.

Keywords: *Crystal Growth; CVT; structure characterization;*

Solid State Chemistry and Nanochemistry

O-521

STRUCTURE PREDICTION AND AB INITIO ENERGY LANDSCAPE EXPLORATION OF PBS AND OF THE PERNITRIDES OF CA, LA AND TI

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A fundamental issue in solid state chemistry and materials science is the rational planning of syntheses.[1] The basic requirements for success in this endeavor are the ability to predict possible target compounds, including metastable modifications at real thermodynamic conditions, and to devise synthesis routes to access these predicted compounds.

Predicting which crystalline modifications can exist in a chemical system requires the global exploration of its energy landscape.[1] Due to the large computational effort involved, in the past this search for sufficiently stable minima has been performed employing a variety of empirical potentials and cost functions followed by a local optimization on the ab initio level. However, this might introduce some bias favoring certain types of chemical bonding and entails the risk of overlooking important modifications that are not modeled accurately using empirical potentials, necessitating the use of ab initio energy functions during the global optimization phase of the structure prediction.

Thus, we have applied a global optimization tool, simulated annealing, to the study of the ab initio energy landscape of PbS [2] and the pernitrides of Ca, La and Ti, exhibiting various types of chemical bonding. For the PbS system, we recover the experimentally known structures, clarify the experimental structures at intermediary pressures, predict the existence of an a-GeTe modification that competes with the known rock salt modifcation at standard pressure and analyze its electronic and vibrational structure and its kinetic stability. For the pernitrides, our explorations confirm the recent discovery of a new CaN_2-modification [3], and predict kinetically stable polymorphs for LaN_2 and TiN_2.

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Keywords: *structure prediction; energy landscape; lead sulfide; pernitride;*

Solid State Chemistry and Nanochemistry

O-522

NEW THERMOELECTRICS BY COMBINATION OF COSB3 WITH GE/SB/TE MATERIALS

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The reduction of the lattice thermal conductivity is the method of choice for improving the figure of merit *ZT* of thermoelectric materials. Inducing nanostructures is one promising way to achieve this, and structures that are heterogeneous on the nanoscale represent an intriguing approach.[Kanatzidis et al., *Angew. Chem. Int. Ed.* **2009**, *48*, 8616.; Zhang et al., *J. Electron. Mater.* **2011**, *40*, 932.]

Nanocomposites of $CoSb_3$ and Ge/Sb/Te (GST) compounds – which both exhibit interesting thermoelectric properties – are a promising class of materials, and their synthesis involves challenging solid-state syntheses. We have shown that the *ZT* values of GST materials strongly depend on the type and distribution of the nanostructures present.[Oeckler et al., *Chem. Mater.* **2011**, *23*, 4349.] Heterostructures of cubic skutterudite-type crystals in a bulk matrix of trigonal GST were obtained by quenching melts of stoichiometric mixtures of the elements, followed by annealing. Quenched samples exhibit interesting features: Over wide regions of the bulk, triangular holes with edge lengths from 0.2 to 1.5 µm are uniformly arranged along parallel lines. In these holes, there are small skutterudite-type precipitates. Subsequent thermal treatment has a great influence on the size and shape of the $CoSb_3$ crystals, in which up to 50 % of the Sb sites are occupied by Ge/Te. In addition, octahedrally shaped aggregates are formed. These consist of grown-together layered heterostructures of GST and $CoSb_3$.

This combination of heterogeneous nanostructures with anion substitution in $CoSb_3$ crystallites may be an intriguing way to further improve thermoelectric characteristics. The skutterudite-type precipitates occur with a variety of crystal morphologies and are firmly intergrown with the matrix. The $CoSb_3$/GST octahedra exhibit well-defined relationships between the crystallographic orientations of their components. The different kinds of heterostructures were analyzed on the atomic level by means of HRTEM.

Keywords: *GST; skutterudite; thermoelectrics; intergrowth; nanostructure;*

Solid State Chemistry and Nanochemistry

O-523

VARYING THE NANOSTRUCTURE OF TERNARY GERMANIUM TELLURIDES AND ITS INFLUENCE ON THERMOELECTRIC PROPERTIES

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Multinary tellurides – especially nanostructured ones – have turned out to be promising novel thermoelectrics with high figures of merit $ZT=S^2\sigma T/k$. In multinary systems, the charge carrier concentration is flexible, allowing one to optimize the Seebeck coefficient*S*. Real-structure effects and nanostructures enhance phonon scattering and thus reduce thermal conductivity k, which means an increase of *ZT*.

At ambient conditions, stable compounds of the "homologous" series $(GeTe)_n(Sb_2Te_3)$ exhibit trigonal layered structures. In the rocksalt-type high-temperature phase, Ge/Sb/vacancies are randomly distributed on the cation sites. The GeTe content n determines both the vacancy concentration in the cubic phase and the thickness of the rocksalt-type slabs in the trigonal phase. In addition to the thermal treatment, this has a strong impact on the nanostructures formed when the diffusion required for the phase transition occurs incompletely. For n = 12 or 19, *ZT* values up to 1.3 are reached.[1] Se and Sn doping result in more pronounced nanostructures at lower n combined with new features probably related to phase separation. In-substituted samples exhibit less short-range vacancy ordering resulting in a less pronounced nanostructure, while Li can be used to stabilize the cubic phase by filling vacancies. Additional Sb sheets in layered phases lead to translation periods of up to 10 nm in (often metastable) compounds like $(MTe)(Sb_2Te_3)(Sb_2)_4$ (M = Ge, Sn).[2]

The average domain size of $GeBi_2Te_4$ quenched under high-pressure (12GPa) depends on the quenching rate. The associated grain and domain boundary effects strongly influence the electrical conductivity σ, which changes form metallic to semiconducting with decreasing domain size and more randomly oriented domains.[3]

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Keywords: *Tellurides; Nanostructure; Thermoelectric;*

Solid State Chemistry and Nanochemistry

O-524

THE ROLE OF DOMAIN SIZE, STRUCTURE AND TRANSFORMATION IN DEFINING P-X-T HYSTERESIS IN HYDROGEN SORPTION BY TRANSITION METAL OXIDES (TON) AND SULPHIDES (TSN) TO FORM HXTON AND HXTSN BRONZES WHEN ACTIVATED BY SPILLOVER

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A non-stoichiometric bronze is a solid formed by intercalation via electron and cation insertion into the host oxide or sulphide. Hydrogen bronzes (H_xTO_n and H_xTS_n) are of particular interest since they contain the smallest guest ion and the consequent high charge density tends to polarize the surrounding host lattice. Following early studies on H_xWO_3 and H_xMoO_3 a considerable number of well-characterised hydrogen bronzes have been prepared from transition metal oxides and chalcogenides with either a layer structures or three dimensional matrices containing tunnels; proton mobilities therein approach those in water.

We describe significant rates and extents of H_2 sorption by transition metal oxides and sulphides in the presence (but not in the absence) of Pt at 323K and 5-101kPa, where anion removal by bulk reduction was not thought to be significant. Preliminary in-situ X-ray diffraction has revealed the development and decomposition of H_xTO_n and H_xTS_n phases as a function of T and p_{H2}. The results are relevant to the optimisation of (**i**) catalysts, (**ii**) reversible electrode materials, (**iii**) electrochromic devices and (**iv**) hydrogen storage.

XRD is an ideal non-invasive technique for probing transformations of such solids. -WO_3 under present conditions is normally monoclinic (and only orthorhombic or tetragonal at higher temperatures). By varying the partial pressure of hydrogen in the presence of activating Pt at a temperature of 323K, WO_3 undergoes reversible phase changes to a tetragonal structure (a = 0.375nm; c = 0.379nm) that exists at 1-40kPa H_2, and thereafter a cubic phase (a = 0.397nm) is found. Upon reducing the p_{H2} tetragonal domains are reformed, one of which is identical to that found in adsorption. Upon flushing for 12h with N2 a orthorhombic structure (a = 0.725nm; b = 0.750nm; c = 0.384nm) is found.

Data are presented on reversible sorption of hydrogen by Pt/MoO_3, Pt/WO_3, $Pt/Mo_yW_{1-y}O_3$, Pt/Na_yWO_3 and Pt/MoS_2.

Special symposium – I

O-116

SUPER BRONSTED ACID CATALYST AND SUPER SILYL ENOL ETHER – RAPID SYNTHESIS OF POLYKETIDES

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Acid is the classical reagent in organic synthesis. Lewis and Bronsted acids can be utilized as more effective tools for chemical reactions by sophisticated engineering such as "designer acids". Needless to say, the ultimate goal of such "designer acids" is to achieve high reactivity, selectivity, and versatility as a useful tool of organic synthesis. Even now, the full potential of acid catalysts has not yet been realized.

We are interested the combination of super Bronsted acid and super silyl group to establish a cascade reaction to generate complex molecules in a single pot. This successive aldol process is a completely new version of the Mukaiyama aldol reaction and provides numerous opportunities to flexible control the stereochemistry of the product molecule with high selectivity. The long-term goal of the project is to assemble a route to polyketides in one-pot using multi-component condensations enabled by unique reactivity of super sily enol ethers and super Bronsted acid catalyst, which will provide basic information for a polyketide synthesizer in the future. The objective of this particular application is to identify how the complex polyketide can be synthesized efficiently and selectively using the second generation of Mukaiyama aldol reactions.

Special symposium – I

O-117

EVOLUTION OF ASYMMETRIC ORGANOCATALYSIS – RETROCATALYSIS AND THE MULTICATALYST APPROACH

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The combination of distinct organocatalysts performing one-pot multistep reaction sequences, *i.e.*, multicatalysis has become a powerful tool in organic synthesis.[1, 2] It allows the synthesis of complex molecules from simple and readily available starting materials, thereby achieving high levels of reaction and resource efficiency.[1, 2] An extension of this concept is a multicatalyst, *i.e.*, an arbitrary catalyst backbone bearing orthogonally reactive catalytic moieties.[2]

Based on a previously developed highly efficient peptide-based acylation catalyst[3] we designed the first member of organic multicatalysts for the one-pot acylative desymmetrization and subsequent oxidation of *meso*-alkane-1,2-diols affording the corresponding α-acetoxy ketones (up to 97% yield and 97:3 d.r.).[4] We term this strategy of reverse catalyst design as *retrocatalysis* (a step oriented approach) to emphasize the close conceptional relation to *retrosynthesis* (a target structure oriented approach).[2, 4]

Recently, we reported a novel multicatalyst equipped with β-aspartate (epoxidation) and π-methyl histidine (acylative kinetic resolution) as catalytic moieties.[5] In conjunction with hydrazinium sulfate (epoxide opening) this catalyst enabled performing a three-step reaction sequence from simple symmetrical alkenes yielding valuable *trans*-alkane-1,2-diols (up to 99 % *ee*) and monoacylated *trans*-alkane-1,2-diols (up to 68 % *ee*; corresponding *S*-values up to 26).[5]

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Keywords: *Organocatalysis; Peptides; Acylation; Sustainable Chemistry;*

Special symposium – I

O-118

SYNTHESIS OF A NON-REDUCING DISACCHARIDE SCAFFOLD FOR NOVEL LIPID A MIMETICS

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Lipid A is a unique glycolipid, which anchors lipopolysaccharides (LPS) in the outer membrane of Gram-negative bacteria. Lipid A, also known as endotoxin, is recognized by the mammalian innate immune system via the Toll-like receptor 4 (TLR4) -myeloid differentiation factor 2 (MD-2) complex.[1]

Lipid A consists of a β-(1-6)-linked di-glucosamine that carries a strain-specific pattern of β-hydroxy- and/or β-acyloxy- long-chain fatty acids at positions 2, 3, 2' and 3' as well as phosphate groups at positions 1 and 4', respectively.[2] The endotoxic activity of Lipid A depends on the number, length and position of acyl chains and on the presence of phosphate groups.[3] Triggering of innate immune signaling by the Lipid A/MD-2/TLR4 - receptor complex might be regulated by application of specifically designed Lipid A analogues and can aid in the discovery of future immunotherapeutics, vaccine adjuvants and anti-inflammatory agents. Based on the three-dimensional arrangement of Lipid A in the crystal structure of the TLR4-MD-2-LPS complex,[4] novel Lipid A mimetics based on a non-reducing 1,1'-α,α-disaccharide scaffold have been developed. To this end, a non-reducing disaccharide, composed of α-D-mannose and α-D-glucosamine carrying a set of orthogonal protecting groups, which allows for subsequent regioselective acylation and phosphorylation has been assembled. To achieve the demanding stereoselective formation of the 1,1'-α,α-glycosidic bond, serveral orthogonally protected D-Man based 1-*O*-imidate glycosyl donors and orthogonally protected D-Glc2N glycosyl acceptors were synthesized and coupled in a TMSOTf-catalyzed glycosylation reaction.

Acknowledgments: *Financial support from FWF (grant P 22116) is gratefully acknowledged.*

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Keywords: *Carbohydrates; Glycoconjugates; Glycosylation; Protecting Groups;*

Special symposium – I

O-119

COMPLEXATION OF PRIMARY AMINES WITH BORANE OR TRIMETHYLALUMINUM

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Trimethylaluminum (TMA) complexes of methyl-, n-propyl-, cyclopropyl-, allyl- and propargylamine were synthesized and their experimental and theoretical properties were compared with the respective amine-borane analogues. It was shown that the amine ligand of an amine-TMA Lewis acid-base complex can be changed by another amine through a 2:1 amine-TMA intermediate in pentane at room temperature. Similar exchange in the case of amine-borane requires more vigorous conditions in line with the calculated relative energy of the respective transition state. The ^{1}H and ^{13}C NMR experiments examining the addition of one or more equivalent amine to the respective Lewis acid-base complex resulted in fast exchange of the amine ligand in the NMR timescale only in the cases of amine-TMA complexes, which could also be caused by similar 2:1 complex formation. However, in gas phase only 1:1 amine-TMA complexes were obtained by ultraviolet photoelectron spectroscopy (UPS). The observed UP spectra indicate that the stabilization effect of the lone electron pair of nitrogen atom in amines during the borane complexation is stronger than that of the TMA complexation. In line with this observation, the destabilization of the σ_{Al-C} orbitals is lower than that of σ_{B-H}orbitals during the formation amine-TMA complexes and amine-boranes, respectively. It was calculated that the CH_4 elimination of the studied amine-TMA complexes is exothermic, which supports the possibility of their use in metal organic chemical vapour deposition (MOCVD) techniques. On the other hand, our experimental conditions are able to avoid this methane elimination, resulting in the first procedure to synthesize primary amine-TMA complexes.

Keywords: *Lewis acids; synthetic methods; NMR spectroscopy; photoelectron spectroscopy; Computational chemistry;*

Special symposium – II

O-120

CHEMICAL CROSS-LINKING AND HYDROGEN/DEUTERIUM EXCHANGE AS AN ALTERNATIVE APPROACH TO STUDYING THE PROTEIN STRUCTURE

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Determination of the three-dimensional structures of proteins has traditionally been realized by X-ray crystallography and NMR spectroscopy. Although these techniques provide high resolution atomic data, they have some limitations.

Chemical cross-linking and Hydrogen/Deuterium (H/D) exchange combined with high resolution mass spectrometry offer an alternative approach to studying the protein structure. This method is fast, is general and uses small amounts of material.

Our aim was to gain insight into structure of NKR-P1A and NKR-P1C protein, important activating receptors which play a key role in eliminating virally infected and tumor cells.

We used homobifunctional cross-linking reagents DSS and DSG (amine-amine coupling) and heterobifunctional cross-linking reagent EDC (carboxyl-amine coupling). Mass spectrometry was used for cross-links identification and furthermore for precise revealing which residues were involved in the cross-link. The residues which were within a certain distance of each other were converted into covalent bonds by the cross-linking reagent and therefore provided distance constraints which were used for protein structure modeling.

In the second approach, H/D exchange combined with mass spectrometry was applied to study the NKR-P1A loop conformation. The aim of this analysis was to compare the kinetics of H/D exchange for NKR-P1A and NKR-P1A in which the loop was removed and replaced with two alanines. H/D exchange revealed that the solution structure differs from the crystal structure in the conformation of the conserved loop. While the conserved loop is in close proximity to compact core in solution, it is extended from the core in the crystal structure where it interacts with the surface of a symmetry-related molecule.

Finally, distance constraints derived from cross-linking and information on local solvent accessibility of proteins derived from H/D exchange have been implemented in the modeling of both receptors.

Acknowledgement: *Financial support by the Grant Agency of the Czech Republic (P207/10/1040) and from the Grant Agency of Charles University (403211/2011 and Project UNCE).*

Keywords: *mass spectrometry; protein structures; structural biology;*

Special symposium – II

O-121

SYNTHESIS OF FERROCENESTRONE

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Ferrocene conjugates with various types of biologically active compounds such as saccharides, steroids or peptides have been studied intensively by bioorganometallic and medicinal chemists in the last few years for their new interesting properties compared to the model compounds.[1, 2] Ferrocifen may serve as a notable example of an interesting new substance. It is a ferrocene containing derivative of tamoxifen with potential effect in treatment of breast cancer.

Although several conjugates of steroids with ferrocene have been prepared, the cyclopentadienyl ring has not been the integral part of the steroid skeleton in any of them. In regard of our recent results concerning new synthesis of estrone,[3] we decided to address the synthesis of first such steroid, containing ferrocene in place of the aromatic A-ring – ferrocenestrone.[4]

The approach to the ferrocene-steroid framework construction was based on transition metal mediated reactions starting from a suitably substituted chiral ferrocene. The methods used were: zirconocene-mediated oxidative additions with successive alkylation sequences, palladium-catalyzed cross-coupling reactions, ruthenium-catalyzed skeletal rearrangements (enyne metathesis), palladium and iridium catalyzed hydrogenations etc. Also selective oxidation and subsequent borane reduction was used for the final change of skeletal configuration. Successful application of the above mentioned methods yielded the first metallocene based steroid derivative.

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Keywords: *asymmetric synthesis; metallocenes; steroids; synthesis design;*

Special symposium – II

O-122

BRASSINOSTEROIDS, SYNTHETIC CHALLENGE FOR HUMAN MEDICINE

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Discovery of brassinosteroids (BS) later recognized as a new class of plant hormones became a historical event indicating versatile role of steroids as hormonal regulators typical to most organisms inhabiting the Earth. BS were found to be very active plant growth stimulants having at the same time adaptogenic and protective properties. As obligatory constituents of plants, BS have been consumed by mammals with food over all the evolution, but their role outside plant kingdom has never been supposed.

Except for toxicological aspects, during the early period of BS investigations there were no attempts to look for their effects in higher organisms. Being chemists, who were lucky to solve the problem of BS availability for practice, and having a large variety of natural BS in our hands, we started systematic studies of BS phenomena in animals quite long ago with expectation to discover their possible role outside plant kingdom. Our first results were reported in Prachatice at 18h Conference on Isoprenoids and published in our monograph in 1999. This was the beginning of extensive research that later got development in many laboratories and brought us to implementation of the obtained results for human and animal use.

The present paper will discuss our results in studies on chemical synthesis, specific properties and natural occurrence of BS that became critically important for their development as a basis for new medications. Among the most interesting results are the findings of regio- and stereoselective approaches to the synthesis of the cyclic part and steroid side chain bearing characteristic functionality, ways for introduction of an isotope label or another modifier into a BS-molecule, which are necessary for analytical and pharmacokinetic studies, and synthesis of new BS-based hybrid molecules having additional pharmacophore, tracer or another group influencing physico-chemical and physiological properties of BS into the desirable direction.

Keywords: *Brassinosteroids; Phytohormones; Synthesis; Medicinal application;*

Special symposium – III

O-123

NEED TO MAKE A BOND? TRY IT IN WATER AT ROOM TEMPERATURE

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New technology for effecting a variety of transition metal-catalyzed cross-coupling reactions under green chemistry conditions; i.e., in water at room temperature, will be described. These are enabled by virtue of the "designer" surfactant TPGS-750-M, which quickly forms nanomicelles upon dissolution in water, in which the reactions take place. Reactions to be discussed include unpublished results on Pd-catalyzed aromatic aminations and Stille couplings, copper-catalyzed conjugate additions, and Zn-mediated halide reductions.

Keywords: *green chemistry; cross-couplings; catalysis;*

Special symposium – III

O-124

STRATEGIES, DESIGN AND SYNTHESIS OF HIGHLY ELECTROLUMINESCENT DEVICES MADE WITH A CONVENIENTLY SYNTHESISED 2-THIENYL-2ʹ-(1H-PENTAFLUOROPHENYL) PYRROLE BUILDING BLOCKS

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Synthesis of new molecules or polymers that have bipolar transport properties and utilization of perfluoroaromatics for molecular recognition has in recent years been an intensely studied topic.

The convenient synthesis of substituted 2-thienyl-2'-(N--pentafluorophenyl)pyrrole derivatives is described from 5-substituted 2-thienylaldehydes by Stetter reaction[1] and bromoacetyl tiophenes (yielding 1,4-dicarbonyl compounds) and Paal-Knorr pyrrole synthesis.[2]

This molecules labeled TP NFB is composed of triphenylamine or carbazole (known to transport holes) and oxadiazole, triazole and pyrazine (know to transport electrons) moieties.

Nucleophilic displacement of a single fluorine atom in pentafluorophenyl group by azide anion affords new possibilities for cross linking, colour incorporating, efficient photosensitive dyes and photolabeling. The target compounds can be used as building blocks for novel materials with optoelectronic properties OLED, fotolabeling reagents or as photosensitizers in the so-called "Gräetzel solar cells".[3, 4]

Acknowledgement: *This work was financially supported by grants from the Ministry of Education of the Slovak Republic No. 1/0660/11 1/1072/11, APVV-0202-10*

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Keywords: *Synthesis design; Polymers;*

Special symposium – III

O-125

RETENTION MECHANISM OF NUCLEOTIDES AND THEIR SEPARATION WITH THE USE OF HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

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Nucleotides are essential for living organisms. They take part in many cellular and intercellular processes, playing important regulatory functions. Their presence and quantity has to be controlled for such purposes as: cardiovascular system monitoring, determination biomarkers of oxidative stress, microorganisms, cellular extracts study, erythocytes, baby foods and human milk determination, food investigation, human cerebrospinal fluid analysis. High performance liquid chromatography (HPLC) became the most popular for the determination of nucleotides. On the other hand although many different packings materials may be used as stationary phases for RP HPLC, generally only octadecyl phase is used for nucleotides analysis. However the resolution and peak shapes of analyzed compounds are often not satisfactory. For this reason the improvement in analysis of nucleic acids components by RP HPLC is of great importance. The simplest way to achieve it, is to change mobile phase composition or stationary phase type.

The main goal of the study was to test variety of HPLC columns to chose the best one for the analysis of polar nucleotides. Two octadecyl columns were used, differing in the carbon load. On the other hand also medium polarity packing material have been utilized, namely: alkylamide, cholesterol and alkyl-phosphate. Phenyl stationary phase was also investigated. Most of these material have been utilized in the separation of nucleotides for the first time. The special attention was paid to the influence of mobile phase buffer pH, since this may be important parameter controlling resolution of nucleotides. Such systematic studies concerning the influence of pH on the retention of nucleotides on specific packings materials was performed for the first time. Obtained results allowed for the selection of the best stationary phase for the separation of nucleotides.

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Keywords: *high performance liquid chromatography; nucleotides; stationary phase;*

Special symposium – III

O-126

FUNCTIONAL MOLECULES BASED ON AROMATIC ARCHITECTURES

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Aromatic architectures have left the world of flat land and taken center stage in supramolecular and materials chemistry. The key parts of molecular machines, the templates for novel graphenoids and fullerenes as well as the active compounds in light-energy devices all start from aromatic scaffolds. Our particular interests in the stereochemistry of novel aromatic morphologies and topologies will be presented with an eye toward understanding their structure, dynamics and function.

Keywords: *Aromatic Chemistry; Materials Chemistry; Supramolecular Chemistry; Stereochemistry; Molecular Function;*

P-0001

SECTOR MODEL SCHEME FOR PLACEMENT OF EXPLICIT WATER MOLECULES FOR PKA PREDICTION

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Accurate prediction of the properties associated with proton transfer reactions, in particular the acidity dissociation constant (K_a), are a benchmark challenge for theory. Considerable efforts have been made in the last decade towards prediction within 0.5 units,[1] which is the minimum level of accuracy for many problems such as structure based drug design.[2] Hybrid approaches, referred to as *continuum cluster* (CC), are the most recent and promising development in pKa prediction.[1, 3, 4, 5] They attempt to capture some of the missing first solvation shell effects by adding a small number (<4) solvent molecules explicitly around the solute embedded in the solvent cavity. However, a number of practical challenges arise in application of this method due to the need to have a consistent framework for determination of optimal number and position of solvent molecules surrounding the solute. We propose a sector model approach to investigate in greater detail the role of explicit first-shell solvation of a set of carboxylic acids and their conjugate bases. This model offers the possibility of systematizing the study of these effects according to the degree of solvation (S_D) and the configuration of solvation (S_C), which allows a number of rules for future prediction to be elucidated. Furthermore, prediction within 1kcal/mol, a chemically significant bound, is demonstrated, for a diverse set of carboxylic acids.

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Keywords: *pKa prediction; continuum cluster; explicit solvent; sector model;*

P-0002

THEORETICAL INVESTIGATIONS ON ELECTRONICS STRUCTURE, AND CHEMICAL BONDING ON IRIDATHIABENZENE AND IRIDAOXABENZNE

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The electronic structure and properties of the Iridathiabenzene and Iridaoxabenzne isomers have been investigated using the hybrid density functional mpw1pw91 theory. The energetic aspect shows that trans-ortho isomer is the most stable isomer. This is compatible with principles of minimum energy and minimum polarizability. Molecular orbital analysis shows a linear correlation between hardness and anisotropic polarizability values for Iridathiabenzene and iridaoxabenzene isomers. The structural and natural bond analysis (NBO) results illustrate electronic delocalization in these rings. Also, the study of non linear optical properties of these molecules indicate a good correlation between b_{tot} and E(HOMO) for iridathiabenzene. The results from natural bond orbital (NBO) analysis have provided insights into Ir–ligand, P-H_{apical} and P-H_{basal} bonding.

Keywords: *Isomers; Bond energy; Analytical Methods; Metallacycles;*

P-0003

THEORETICAL STUDIES OF METALLOPHILIC INTERACTIONS THROUGH THE USE OF LOCAL CORRELATION METHODS

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It has long been observed that cationic Au(I)d^{10} complexes can establish weak metal-metal interactions. This effect is somewhat curious, since it involves centers with the same charge and completely filled electronic shells. Similar interactions are found in complexes with Ag and Cu, but with a much smaller magnitude. This effect has come to be known as aurophilicity, and is strongly linked to electron correlation with a further strengthening by relativistic effects.[1] Previous theoretical works have shown that high levels of theory are required to reproduced this effect quantitatively (e.g. CCSD(T)).[2]

We have performed a series of calculations on inorganic complex dimers of the type $(Cl\text{-}M\text{-}X)_2$, with M = Au, Ag. Comparison is made to density functional theory (DFT), including empirical dispersion corrections, and state of the art wave function-based methods. Local approximations have also been used to treat the metal sites at the highest level of theory in a QM/QM hybrid scheme.[3] We show some of the challenges in the theoretical treatment of aurophilic interactions, with prospects on the treatment of further metal-metal interactions in bioinorganic complexes.

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Keywords: *Ab initio calculations; Aurophilicity; Electronic structure;*

P-0004

MOLECULAR DYNAMICS SIMULATIONS OF BIOACTIVE GLASS NANOPARTICLES

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Bioactive glasses such as the 45S5 composition (BG45) are clinically employed as bone defect fillers in orthopaedic and dental applications. Their potential in regenerative medicine has also been highlighted but not exploited as yet, due to the lack of fundamental understanding of their composition-structure-activity relations. For instance, nanosized BG45 particles have shown enhanced biological activity and antibacterial properties, which could be the key towards developing a new generation of biomaterials for regenerative medicine. However, the rational development of these materials requires a better understanding of the origin of the superior properties of BG45 nanoparticles. Molecular dynamics simulations of a Bioglass spherical nanoparticle (approximately 6 nm diameter) have been carried out to investigate how the reduced size affect structural and dynamical features, which could enhance the bioreactivity of these systems. Compared to the bulk glass or to the 2D-flat surface of BG45, the simulations reveal that the reduced size leads to a further slight reduction in the already low silicate connectivity on the nanoparticle surface, to a ring size distribution shifted towards three-membered rings, and to a higher Na^+/Ca^{2+} ratio in close proximity of the surface. A higher mobility of Na cations in the external regions of the nanoparticle has also been detected. The possible ways in which these effects can translate into higher bioreactivity of BG45 nanoparticles are discussed.

Keywords: *Molecular dynamics; Nanoparticles; Glasses; Surface chemistry; Structure-activity relationships;*

P-0005

CALCULATION OF 4-BIT NUMBERS WITH AN ALLOSTERIC INDICATOR DISPLACEMENT ASSAY

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Logic gates, better known as the Boolean operations, perform all fundamental logical circuits in electronics. In addition, molecular logic is becoming increasingly important.[1-2] In our work we have developed a 4-bit full adder system which allowed us to sum up two 4-bit numbers on the basis of the IMPLICATION-gate (IMP-gate).[3] We used a two-component saccharide probe for the generation of the IMP-gate which follows the principle of an allosteric indicator displacement assay (AIDA).[4] In detail the main fluorescence signal was provided by an anionic fluorescence dye HPTS which retains in the presence of fructose and decreases by the addition of quencher component BBV. In the case of quencher and fructose being added the fluorescence reaches its original intensity. For the summation of two 4-bit numbers four full adder units containing two half adder units each were connected in a row by suitable conjunction of the IMP and FALSE operation. The correct binary values of the total 4-bit sum were obtained after 8 hours of preparation.

Furthermore it is possible to establish the sum of numbers larger than 4-bit which is only limited by the size of the used wellplate. Also other operations such as subtraction and multiplication have been done.

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Keywords: *Molecular logic; Saccharide probe; Allosteric indicator displacement assay; Logic gate; Fluorescence quenching;*

P-0006

SEMI-SYNTHESIS AND ABSORPTION PROPERTIES OF ARTIFICIAL BETALAINS

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Betalains are natural pigments classified as yellow betaxanthins or violet-red betacyanins. They originate from spontaneous non-stereoselective addition of amines or amino acids to betalamic acid. Betaxanthins are responsible for visible fluorescence of flowers,*e.g.*, yellow varieties of *Mirabilis jalapa* (four o'clock), whereas betacyanins are natural phenolic antioxidants. In this work, we describe the semi-synthesis of artificial betalains derived from substituted anilines and the experimental and theoretical study of their absorption properties. Eleven derivatives were prepared, purified and the absorption spectra were registered at room temperature in aqueous acid media (pH = 4,5). The absorption maxima (λ_{max}) of all compounds are in the green region of the spectra (510 – 520 nm). The molar absorption coefficients (ε) were determined using second derivative spectroscopy and were found to be between 2.8 and 5.5×10^4 L mol^{-1} cm^{-1}.

The geometry of all derivatives where fully optimized at the DFT SMD(water)/M06-2X/6-31+G(d,p) level. Electronic transition energies and oscillator strengths of the molecules were calculated employing the semiempirical ZIndo/S method considering water as solvent using the SMD solvation model. Theoretical electronic transitions are in good agreement with the experimental values (error in $\lambda_{max} < 3\%$). All compounds studied belongs to the C1 point group and the observed high intensity bands in the visible region arises from HOMO–1?LUMO and HOMO®LUMO transitions and were assigned as π?π* transitions. These results indicate that the substitution pattern in the aromatic iminic portion of such betalains has minor importance in their absorption properties.

Keywords: *betalain; DFT; natural pigment;*

P-0007

AB INITIO BASED METHODOLOGIES FOR INVESTIGATION OF CHARGE TRANSFER THROUGH ORGANIC MOLECULES

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The study of charge transfer (CT) reactivity through organic molecules presents vast opportunities to understand and design materials with desirable electronic properties. In the current work, a first principles methodology has been developed for the evaluation of CT properties in nonadiabatic systems, and implemented into the widely used *ab initio* computational suite GAMESS. In this implementation a broad range of levels of theory, including semiempirical, Hartree-Fock, DFT, or MP2, may be applied to the system studied, to achieve the highest possible accuracy for the size and complexity of the CT system at hand. The calculation of the electronic coupling between an electron donor and acceptor utilizes a localized molecular orbital effective Hamiltonian[1], relating the coupling between the donor and acceptor through the remaining bridge localized orbitals. Furthermore the possible tunneling pathways available are calculated by means of a Greens function matrix of the bridge localized atomic or molecular orbitals.[2] These evaluations shed new light on discussions of through-bond and through-space coupling effects. The electronic coupling and pathway analyses enable a quantification of the magnitude of through-space or through-bond coupling, and clarify through which molecular orbitals these interactions are made possible. Additionally the impact of solvent to these CT characteristics is considered in the present work. Through these investigations, an understanding is gained of the impacts of structure, and presence of functional groups on the donor, acceptor or bridge, on the probability and mechanism of the CT reactions, contributing greatly towards the design of materials, which will offer desirable properties.

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Keywords: *Ab initio calculations; charge transfer;*

P-0008

PHOTOPHYSICAL DYNAMICS OF A RUTHENIUM POLYPYRIDINE DYE CONTROLLED BY SOLVENT PH

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The photophysical properties of the novel trisheteroleptic Ruthenium dye $[Ru(tmBiBzIm)(dppz)(tbbpy)]^{2+}$ (tmBiBzIm = 5,5',6,6'-tetramethyl-2,2'-bibenzimidazole, dppz = dipyrido[3,2-a:2',3,3'-c]phenazine, tbbpy = 4,4'-di-tert-butyl-2,2'-bipyridine) are investigated. The dye structure combines the pH sensitiviy of the bibenzimidazole ligand with the DNA-responsive properties of the dppz ligand. Therefore, the complex might form the basis to develop systems for intracellular DNA and pH sensing.

The combination of these different ligands allows for controlling the photophysics by two distinct mechanisms: (**i**) (de)protonation of the tmBiBzIm and (**ii**) hydrogen bonding to the phenazine-nitrogens of the dppz ligand. A combination of resonance Raman spectroscopy, to reveal the participation of the different ligands in the initial excitation,[1] and fs time-resolved transient absorption measurements, to observe the following development of the photoexcited complex was applied.

As is reported, deprotonation of the tmBiBzIm ligand causes a bathochromic shift of the metal-to-ligand charge-transfer transition although the tmBiBzIm ligand itself does not directly contribute to the light absorption. Furthermore, tmBiBzIm deprotonation shortens the overall excited-state lifetime of the complex significantly. The overall photoinduced dynamics is dominated by the dppz ligand.[2, 3] Consequently, addition of water to the solvent affects the excited-state relaxation pathway as known from, e.g., $[Ru(phen)_2dppz]^{2+}$ (phen = 1,10-phenanthroline) complexes, anticipating similar DNA-responisve properties.

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Keywords: *Laser spectroscopy; Ruthenium; DNA; Raman spectroscopy; Luminescence;*

P-0009

ATMOSPHERIC CHEMISTRY OF METHYLENEIMINE

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A CO_2 post combustion capture test facility employing amine technology is now in operation at Mongstad, Norway. Given the scale of implementation of post-combustion Carbon Capture and Storage CCS, it is likely that there will be relatively small but still significant discharges of amines to the atmosphere during operation of a full-scale plant. There is also the potential for larger scale accidental discharges. CH_3NH_2 and $(CH_3)_2NH$ are among the process degradation products of the more complex amines used in CO_2 capture, and these small amines will therefore always be emitted with the cleaned flue gas to the atmosphere no matter which parent amine is used in the absorber.

Methyleneimine, CH_2NH, and ethyleneimine, CH_3CHNH, is identified as a major photo-oxidation product in the atmospheric degradation of CH_3NH_2 and $(CH_3)_2NH$, respectively. Possible atmospheric sinks of these imines include reactions with OH, NO_3, Cl, O_3 and hydrolysis.

Results from a quantum chemical study of reactions of methyleneimine relevant to tropospheric conditions are presented. Our results indicate that it reacts very rapidly with OH and Cl, and that HCN is formed as a major product.

Keywords: *Ab initio calculations; Kinetics; Atmospheric chemistry; Radical reactions; Environmental chemistry;*

P-0010

QM/MM SIMULATIONS ON ANION COMPLEXES OF A POSITIVELY CHARGED TETRA-TRIAZOLIUM MACROCYCLE

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Anions play an important role in many biological and chemical processes. Many receptors have been synthetized for their recognition, although the efficient recognition of anions, especially in aqueous solution is still very rare. In spite of their high potential, the use of macrocycles incorporating triazole moieties in anion recognition is almost unexplored. Those macrocycles can be positively charged by alkylation polarizing the heterocycle's C-H bond and increasing the electrostatic interactions between the anion and receptor.[1, 2]

The current work reports the theoretical investigations carried out on the binding affinity of a tetra-triazolium macrocycle with a positive net charge of +4 with Cl^-, Br^-, F^-, I^- and SO_4^{2-} anions in the competitive 1:1 DMSO:H_2O solvent mixture. These studies were performed by classical molecular dynamics simulations followed of quantum mechanics/molecular mechanics (QM/MM) simulations using the Amber software.[1] In the QM/MM simulations the macrocycle and the anions (QM region) were treated by quantum mechanics using the semi-empirical PM3 method, while the solvent region composed of TIP3P water molecules and full-atom model of DMSO molecules, were described by classical molecular mechanics.[3]

The results showed that C-H···X hydrogen bonds have an important role in the selective binding affinity macrocyle for the halide and sulphate anions.

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Keywords: *QM/MM simulations; anion recognition; macrocycles; hydrogen bonds;*

P-0011

THE CONNECTION BETWEEN MACROSCOPIC AND QUANTUM PROPERTIES OF ALKANES

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The estimation of physical-chemical properties of alkanes is essential in the theory of chemical structure of substance and engineering practice. Physical-chemical properties (PCP) of normal and iso- alkanes are most extensively studied.

We have ascertained quantitative appropriatenessys between macroscopic properties of alkanes and characteristics of their electronic structure:

$$Z=a_{i}.\bullet e^{\beta i\bullet E}$$

where Z - physical-chemical property (for example, boiling point, molecular weight, density, ets.); α_i and β_i – suitable empirical coefficients, which depend on topological index of chemical structure; E - characteristic of their electronic structure (calculated values of highest occupied and lowest unoccupied molecular orbitals energy, ionization potential (IP) and electron affinity, as well as the width of conducting band).

In series of n-alkanes C_1-C_{10} best correlations may be observed for calculated values of highest occupied and lowest unoccupied molecular orbitals energy, as well as the width of conducting band with macroscopic PCPs. Designed values for IP of n-alkanes C_1-C_{10} were confirmed by outcome of experiment by photoelectron spectroscopy (PES). Received relationship for n-alkanes C_1-C_{10} is confirmed by statistical data manipulation, have correlation coefficient $R = 0{,}95 \div 0{,}99$.

In homologous series of iso-alkanes C_4-C_{10} similar nature of PCP and electronic structure characteristics relations is confirmed for calculated values of highest occupied molecular orbital energy. It may be presumed, that direct analysis (instrumentations) of IP by photoelectron spectroscopy method will confirm the results of quantum-chemical computations.

Received relationship for iso-alkanes is confirmed by statistical data manipulation, have correlation coefficient $R = 0{,}89 \div 0{,}96$.

The existence of such correlations means the availability of the concept of physical-chemical properties forecasting direct from quantum computations and photoelectron spectroscopy data.

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Keywords: *alkanes; ionization potentials; quantum chemistry;*

P-0012

ULTRAFAST CIRCULAR DICHROISM INVESTIGATION OF THE RING OPENING IN 7-DEHYDROCHOLESTEROL

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UV-femtosecond time-resolved circular dichroism (TRCD) spectroscopy has been used to study the ultrafast changes of chirality in a small molecular biological paradigm sample, 7-dehydrocholeserol (7-DHC). Upon UV-photoexcitation, 7-DHC undergoes a ring opening to produce previtamin D_3 and two of the chiral centers of 7-DHC are removed, which impacts the overall chirality of the molecule. Here, measurements of this chirality change connected to the ring opening of 7-DHC with a time-resolution of 280 fs are reported. With this method a previously described discrepancy concerning the photophysics of 7-DHC was clarified. With our set-up the relaxation time of the chirality change was measured to be 1-2 ps, which corresponds to the shortest time-constant in the transient absorption (TA) measurements, allowing us to assign that time-constant to the ring opening.

Acknowledgement: *Financial support by the German Science Foundation (Di 1517/2-1) is gratefully acknowledged.*

Keywords: *Circular dichroism; Vitamins; Time-resolved spectroscopy;*

P-0013

CRYSTAL SHAPE RECOGNITION SOFTWARE

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The X-ray structure determination has seen fast development over last twenty years from a special method towards a semi-automatic tool available to any sufficiently trained scientist. Despite the advancements in both the instruments and methods, some materials still resist the routine approach. Typical examples are highly absorbing minerals containing heavy elements, but high absorption is also encountered with moderately heavy elements measured with copper radiation.

Although the commonly accessible diffractometer programs usually contain tools for absorption correction, details of their functionality are unknown. Moreover, such absorption correction cannot be undone and repeated in later stages of structure solution when the data are processed by different software. For this reason we have started a project[1] of moving absorption correction tools into Jana2006 software.[2] Here we present the first successfully finished part, a tool for automatic shape indexing.

The presented Crystal shape recognition software uses as an input photographs of the crystal shape acquired for various orientations of the sample with the program Crysalis[3], which is delivered for laboratory diffractometers produced by Agilent (former Oxford Diffraction). Our software automatically assigns *hkl* indices to bordering planes, based on the contrast between the image of the crystal and the background. For small samples where the pixel size limits the precision of the mouse movement, this method is more precise. In the next step, the user can make manual corrections of the preliminary shape with a step unlimited by the resolution of the frame. Currently, we are implementing this program to the Jana2006 software[2].

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Keywords: *absorption correction; crystallographic computing; Jana2006;*

P-0014

CONTROLING THE REGIOSELECTIVITY IN THE EXOHEDRAL FUNCTIONALIZATION OF FULLERENES BY SUCCESSIVE FULLERENE REDUCTIONS

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Regioselectivity in the exohedral functionalization of fullerene and endohedral metallofullerenes (EMFs) species widely depends on the nature of the fullerene species and the metallic cluster encapsulated. This regioselectivity can change dramatically from the empty fullerene to the EMF derivative. As we have shown in previous studies on the C_{78} case, both geometric and electronic effects[1–3] due to the presence of the metallic cluster play an important role in the regioselectivity of the reaction when the reactivity of an EMF is compared to that of the free fullerene. It is found that the electronic effects that change the shape and energy of the LUMOs are the most important.[4]

In this work,[5] we present a study on the effect of successive reductions of C_{60} on the regioselectivity of the Diels-Alder, 1,3-dipolar and carbene additions to the fullerenic C_{60} cage. We show that by tuning the number of electrons added to the fullerene, the regioselectivity of the studied reactions changes from the usual [6,6] addition in neutral species to addition to the [5,6] bond when the number of electrons added to C_{60} increases. We also show that changes in aromaticity of the six- and five-membered rings of C_{60} during the reduction process helps to understand the change of the regioselectivity. Our study provides a good model to describe what is happening when a metallic atom or cluster is encapsulated inside a fullerene cage (endohedral metallofullerenes, EMFs), as metal clusters formally transfer a certain number of electrons to the fullerene cage.

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Keywords: *Regioselectivity; fullerenes; Reduction; Density functional calculations; cycloadditions;*

P-0015

ADSORPTION OF HERBICIDE NICOSULFURON ON ACTIVATED CARBON, ALUMINA AND SILICA

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Nicosulfuron, $C_{15}H_{18}N_6O_6S$, belongs to the sulfonylurea's group of the herbicides, widely used in agriculture. We studied the possibilities to remove nicosulfuron from aqueous solution by adsorption on commercial activated carbon, alumina and silica. The adsorption has been investigated at room temperature applying batch equilibrium techniques. The influences of sorption parameters: contact time, solution pH, initial nicosulfuron concentration were studied in order to optimize the reaction conditions.

The investigations showed that adsorption on activated carbon is fast and complete: in less than 5 minutes 100% of the initialy present nicosulfuron was adsorbed.

Nicosulfuron uptake on alumina was evaluated using the Freundlich isotherm model. Freundlich constant, k_F, and heterogenity factor, $1/n$, are calculated from the intercept and slope of the Freundlich linear plot. Knowing the $k_F = 1.0352$ mg/g, one can calculate free energy change $\Delta G = -16.91$ kJ/mol. The negative ΔG value indicates the feasibility of the process and the spontaneous nature of adsorption. The numerical value of $1/n = 0.9651$ indicates an adsorptive process that only slightly suppressed at lower equilibrium concentrations ad is atributed to a heterogeneous nature of the adsorbent's surface without any interactions between adsorbed molecules.

The adsorption isotherms of nicosulfuron on silica with different pore size (18-32, 32-64 and 64-100 ?) seem to indicate adsorption into two steps, where a second monolayer adsorption starts after the first monolayer is completed. This successive adsorption corresponds to the adsorption on surface sites that are structurally different. At low nicosulfuron concentration adsorption only occurs on one kind of sites. As the equilibrium concentration increases, these sites become saturated and other sites contribute significantly to the adsorption.

P-0016

STRUCTURE OF CYTOCHROME P450 1A2-CYTOCHROME B5 BINARY COMPLEX PREDICTED AND EVALUATED BY MEANS OF MOLECULAR DYNAMIC METHODS

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Cytochromes P450 (CYPs) represent a large group of enzymes oxidizing drugs and chemical carcinogens. Eukaryotic CYPs interact with other membrane proteins located in the endoplasmic reticulum. Cytochrome b_5 (cyt b_5), which is also present in endoplasmic reticulum (ER), may enhance, inhibit or have no effect on enzymatic activity of CYPs, depending on the particular CYP isoform and the substrate. Hence, the cyt b_5 has the potential to significantly modulate CYP mediated metabolism of xenobiotics. The cyt b_5-mediated modulation of CYP activity is attributed to the formation of specific protein-protein interaction. Exact 3D structure of the binary complex has not been experimentally determined. However, indirect data based on mutagenesis studies and chemical cross-links indicate that the convex and acidic surface of cyt b_5 binds to the basic concave surface of a CYP.

The study is focused on prediction of the CYP1A2-cyt b_5 binary complex structure, using contemporary methods of theoretical chemistry. In the first step, flexible protein-protein docking method implemented in HADDOCK software was employed to obtain a set of plausible orientations of soluble domains of both cytochromes. Further several individuals were selected according to rough estimations of binding energies and mutual orientations of both protein structures. These binary complexes were subjected to stability evaluation using classical molecular dynamic method implemented in NAMD software. Further we employed steered molecular dynamic protocol. This method was used in order to compare binding free energies of individual CYP1A2-cyt b_5 complexes obtained by protein-protein docking.

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Keywords: *cytochrome p450; cytochrome b5; molecular modeling;*

P-0017

THEORETICAL INVESTIGATION OF THETA4 FOR TWO NANOMEMBRANES IN VARIOUS DIELECTRIC ENVIRONMENTS

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Atomic-level molecular dynamics data for dipalmitoyl phosphatidylcholine (DPPC) and dimyristoyl phosphatidylcholine (DMPC) are approved that they have such an important role in nano biotechnology sciences so that they are important for new researches. These phosphatidylcholines are used to industry of drug delivery and etc. Gaussian software calculated different quantum descriptors for each molecule. we used ab initio 6-31G method for multiple linear regression, factor analysis-based multiple linear regression, principal component regression and partial least squares combined with genetic algorithm for variable selection were employed to make connections between structural parameters and stability activity. The effect of dielectric coefficient differences is fully studied in different critical temperatures, such as Manufactory, body temperature, and fever.

In the present work, we considered the interaction between polar head groups and hydrophobic strains of DPPC/DMPC with polar molecules systems like water, ethanol and etc. by different dielectric coefficient that extended our ab initio calculations to determine the minimum energy conformation of the DPPC/DMPC structures. The method that has been used is initial Hortree Fock computation, STO-3G level to optimize the molecules in different solvents environments by different dielectric coefficients as well. The results elaborated that the phospholipids in ethanol and water are more compatible than the other solvents so that the supposed dielectric coefficient is appropriate to construct the PCs as well; In addition the dihedral angle mentioned in the article is the same as the energy that the pressure on the tails in ethanol and water is more than the other solvents. Thus, the ethanol and water seem more persuadable to use as the solvent in the bio molecular technologies and the most convenient for the biologic environments either in vitro and in vivo.

Keywords: *Nanomembrane; ab initio 6-31G method;*

P-0018

ELECTRICAL CONDUCTIVITY OF SOLUTIONS OF SOME ELECTROLYTES IN MIXTURES OF WATER WITH 2-METHOXYETHANOL AT THE TEMPERATURE 298.15 K

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The electric conductivities of solutions of NaBr, NBu_4Br, $NaBPh_4$, KBr and KCl have been measured a wide concentration range of binary mixtures of water (1) – 2-methoxyethanol (2) binary mixtures were measured at T = 298.15 K. In the case of KCl and NaCl (due to of the low solubility of these electrolytes) our studies have been carried out in mixtures containing a maximum of 2-methoxyethanol equal $x_2 = 0.5$, respectively. For measurements the apparatus of high accuracy has been used. For the analysis of the dependence molar conductivities (Λ) on the concentration of the electrolyte Fuossa-Justice equation has been applied (using a nonlinear least-squares method). We have found values ??of: limiting molar conductance of electrolytes (Λ_0), ionic association constants (K_A) and the distance parameter of ions (R). The values of Walden product (Λ ? η) have been also calculated. Based on the Fuoss-Hirsh assumption, the limiting molar conductance of individual ions have been calculated. The changes of values of all these parameters have been analyzed as a function of the composition of the studied mixtures in terms of ion - ion and ion – solvent interactions.

Keywords: *Electrical conductivity; Binary mixtures; Association constant;*

P-0019

ELECTRIC QUADRUPOLE MOMENT OF GRAPHENE AND ITS EFFECT ON INTERMOLECULAR INTERACTIONS

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Understanding the nature of graphene...solvent interactions might help to design new and more efficient solvents for liquid-phase graphene exfoliation. Here we focus on the electrostatic component of interaction energy. Carbon atoms in a graphene sheet exhibit permanent quadrupole moment due to the aromatic pi electron distribution. In an infinite graphene sheet the electrostatic field of the atomic quadrupoles sums to zero and therefore does not contribute to intermolecular interactions. However, for a finite model, this field is nonzero and vanishes only very slowly with model size. Here we investigate magnitude of the graphene quadrupolar field as a function of model size and its influence on intermolecular interactions. Molecular dynamics simulations were carried out with and without explicit quadrupolar field and potentials of mean force are derived, compared and discussed.

Keywords: *graphene; electrostatic interaction; density functional calculations; molecular dynamics;*

P-0020

ESTERIFICATION OF ACRYLIC ACID WITH 2-ETHYLHEXAN-1-OL THERMODYNAMIC AND KINETIC STUDY

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2-Ethylhexyl acrylate is obtained by direct esterification of acrylic acid with 2-ethylhexan-1-ol. It is reversible and endothermic reaction, running in the presence of an acid catalyst. Sulfuric acid or methanesulfonic acid are the most commonly used catalysts in the industrial processes. However, they are generate heavy waste difficult to separate from the product. Solution to these problems can be use of an efficient heterogeneous catalysts.

Designing the esterification in an industrial scale requires accurate thermodynamic and kinetic parameters to be determined. The solid acid catalysts in the form of sulfonated polystyrene/divinylbenzene resin are well recognized to be active and durable industrial catalysts. So far, the kinetic of acrylic acid esterification with 2-ethylexan-1-ol in the presence of acidic ion exchange resins has been scarcely documented in the literature.

The reaction equilibrium was studied for equimolar alcohol to acid mixture in the presence of Amberlyst 70. The reaction enthalpy was estimated from linear dependence of equilibrium constant on reciprocal temperature in the range of 333 – 373 K.

The esterification reaction rate was determined for various ratio of acid to alcohol and temperature range of 353 – 393 K. It was checked that to eliminate mass transfer limitations, it is sufficient to continuously stir the reaction mixture at a rate of 500 rpm. The effect of catalyst loading was tested as well.

The apparent (K_x) and thermodynamic equilibrium constant (K_a) was estimated by the UNIQUAC method. It was found that, reaction was first-order both in the presence of acid excess as well as in the alcohol excess. A quasi-homogenous kinetic model was used to describe the reaction. It was taking into account both mole fractions and activities to describe nonideality of liquid phase. Kinetic parameters were found.

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Keywords: *Ion exchange resins; acrylates; equilibrium constant; kinetic parameters;*

P-0021

CHEMISTRY INSIDE MOLECULAR CONTAINERS IN THE GAS-PHASE

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The reversible complexation of guests by supramolecular hosts affects their chemical reactivity in solution,[1–3] affording impressive examples of supramolecular catalysis and, in the case of reactions inside concave hosts, biomimetic activity.[4–8] In the gas phase, however, the situation is different – the supply of thermal energy favors irreversible dissociation rather than chemical reactions of the encapsulated guest.[9–11] While precedents for gas-phase reactivity of host-guest complexes exist,[12–19] inner-phase reactions have until now been limited to the solution phase.[20]

We studied host-guest inclusion complexes of cucurbit[*n*]urils (CB*n*, *n* = 6, 7, 8) and three water-soluble bicyclic azoalkane homologues in gas phase, we additionally performed quantum chemical calculations, and we found several examples of thermally activated, selective retro-Diels-Alder reactions in the gas phase. We observed an interesting reactivity pattern, where the cycloreversion inside the cavity becomes dominant when the packing coefficient[35] of the complexes fall within a narrow range. We derived a potential function in the form of a Lennard-Jones 12-6 potential to model the interaction of such spherical guests positioned centro-symmetrically inside a host cavity.

Efficient inner-phase reactions for some, but not for all homologous complexes, disclosed fundamental insights into the factors governing chemical reactivity in isolated confined environments. We interpret the observed trends in terms of an interplay of three factors: (**a**) the intrinsic activation energies for chemical reaction of the guest, (**b**) the constrictive binding displayed by the particular host, and (**c**) the void space inside the host-guest complex.

A combination of constrictive binding and void space emerges as an important structure-reactivity relationship. The two effects should directly manifest themselves on the pre-exponential factors and activation energies of the inner-phase reaction and, therefore, be transferable to catalysis and biocatalysis inside confined reaction space.

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Keywords: *inner-phase reactions; gas-phase; host-guest;*

P-0022

ELECTRIDES, NONLINEAR OPTICAL PROPERTIES AND VIBRATIONS

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Electrides are ionic compounds in which electrons behave as anions. These special electrons are separated from any nuclei, occupying positions typically populated by anions in ionic compounds. It is well-known that electrides have very large NLO electronic properties.[1–4] The main goal of this study has been to determine and analyze the vibrational, as compared to the electronic, NLO properties for a representative set of electrides including Li@Calix, Na@Calix, $Li@B_{10}H_{14}$, $Li_2^{\bullet+}TCNQ^{\bullet-}$ and $Na_2^{\bullet+}TCNQ^{\bullet-}$. Our results, obtained by UB3LYP level using different Pople basis set, vary depending upon the electride and the NLO process. In general, however, we find that the average static vibrational first and second hyperpolarizability exceed the corresponding electronic property values, sometimes in the latter case by more than an order of magnitude. As far as dynamic properties are concerned, on average they are roughly the same as the corresponding static electronic hyperpolarizability, and in particular cases they may be twice as large or more. The role of anharmonicity in the (NR) hyperpolarizabilities is variable. It plays a dominant role for the $Li@B_{10}H_{14}$ first and second hyperpolarizability, but is negligible for the $Li_2^{\bullet+}TCNQ^{\bullet-}$ first (though not the second) hyperpolarizability.

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Keywords: *electride; Non linear optical properties; hyperpolarizabilities; vibrational contributions;*

P-0023

SOLVENT AND IONIC STRENGTH EFFECTS ON THE STABILITY OF DIOXOVANADIUM (V) COMPLEXES WITH IDA AND DTPA

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Our laboratory has taken up the study of complexation of various aminopolycarboxylic acids with VO_2^+ and MoO_4^{2-} ions in order to study the influence of the solvents and ionic medium and to determine the contribution of Kamlet-Abboud-Taft (KAT) parameters in recent years.[1–3] Polarity of a liquid is defined as the sum of all possible specific and non-specific interactions between the solvent and a potential solute. The goal of this study is to investigate the H_2O-CH_3OH composition and the ionic strength influences on the stability of dioxovanadium (V) + iminodiacetic acid (IDA) and dioxovanadium (V) + diethylenetriaminepentaacetic acid (DTPA) complexes respectively. UV data have been gathered at a fixed ionic strength ($I = 0.1$ mol.dm^{-3} of sodium perchlorate) and t = 25°C for the solvent effect study. Complexation of VO_2^+ ion with DTPA was studied at different ionic strengths of sodium chloride ($0.1 \leq I$ / mol.dm^{-3} ≤ 1.0). It was concluded that the increase in the hydrogen-bond acceptor capability of the solvent favors a higher thermodynamic stability of the products with respect to the reactants and consequently, an increase in the corresponding stability constants. Determination of the activity coefficients of aqueous electrolyte solutions is a very important area of research. At higher concentrations short range and non electrostatic interactions have to be taken into account, and this is usually done by adding terms to the Debye-Hückel expression. The most popular models are the Pitzer and specific ion interaction theory (SIT) equations. The errors and R^2 values for the models showed that the SIT model is the best for this research.

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Keywords: *Thermodynamics; Solvent effects; Hydrogen bonds; UV/Vis spectroscopy;*

P-0024

CALCULATION OF ELECTRONIC EXCITATION ENERGIES THROUGH THE USE OF INCREMENTAL CORRELATION SCHEMES

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The application of ab initio correlation methods is severely hindered by their computational cost. The exponential scaling of the latter relative to the system size only allows for the treatment of relatively small systems. However, electronic correlation in molecules is known to be a short range effect, and significant savings can be obtained by taking this into account, may it be through the use of integral screening,[1] local approximations[2] or many-body approaches. The latter class of methods works by splitting the system into fragments and computing the energy as a many-body expansion. Such approaches have been applied to the ground state correlation energy of molecular systems.[3] We have also recently presented an extension for the calculation of excited states.[4]

In this work, the incremental scheme is applied in the calculation of excitation energies of a large benchmark set. We present several improvements to the method including new robust criteria to identify the main fragments involved in the excitation. Results show that the method is capable of reproducing full calculation results in only a fraction of the total computational time. Preliminary applications in the study of physisorbed molecules are also discussed.

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Keywords: *Electronic structure; Ab initio calculations; Photochemistry;*

P-0025

MULTICENTER BOND INDEX: A VERSATILE TOOL TO CHARACTERIZE ELECTRON DELOCALIZATION AND AROMATICITY.

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Multicenter indices (MCI)[1–10] are used in a number of situations such as the analysis of conjugation and hyperconjugation effects,[7] to identify agostic bonds, to account for electron distributions in molecules[4–5] or to study aromaticity in both organic[9] and all-metal compounds.[4–11] The formula of MCI involves the intuitive *n*-order central moment of the electron population,[12–13] which depends on the *n*-order RDM. The calculation of the *n*-RDM is overwhelmingly expensive for correlated wavefunctions and, therefore, there are so few studies of MCI available in the literature. In this talk we review the applications of MCI and suggest a new approximation for the 3-RDM that provides more accurate MCI values than the approximations suggested thus far in the literature.[15–16]

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Keywords: *mutiple bonds; aromaticity; bond theory; agostic interactions;*

P-0026

EXPLORING THE NATURE OF CARBOHYDRATE-AROMATIC DISPERSION INTERACTIONS VIA SOPHISTICATED COMPUTATIONAL CHEMISTRY TOOLS

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Interactions of saccharides with receptors belong to the most important ones. The carbohydrates represent signalling molecules from so-called glycocode, which is recognized by the variety of proteins. There are several ways how saccharides interact with proteins. The role of dispersion-driven CH-π interactions in protein-carbohydrate interactions has been underestimated for a long time. This type of interaction occurs between carbohydrate apolar faces and aromatic amino-acids.

We introduce first systematic study of CH-π interactions between carbohydrates (β-D-glucopyranose, β-D-mannopyranose, α-L-fucopyranose) and aromatic amino-acid models: benzene and naphtalene. 3D interaction energy (E_{int}) scan was performed to elucidate interaction energy maps for carbohydrate-benzene interaction. Resulting stationary complexes were reoptimized and their E_{int} was refined at highly-sophisticated level. To study possible degree of additivity, we used geometries of carbohydrate-benzene complexes to build-up monodentate (interaction with one CH-group) and bidentate (interaction with two CH-groups) carbohydrate-naphtalene complexes.

Results show E_{int} in carbohydrate-benzene complex up to -5,40 kcal/mol. We localized most attractive regions where the E_{int} is highest. The strongest interaction is localized above and under CH-groups of carbohydrate. Additionally, benzene can recognize the specific hydrogens of carbohydrate in specific ideal distance (|(C)H-π| distance around 2,3 ?). The aromatic ring is coplanar with the carbohydrate cycle.

Localization of the strongest interaction regions for carbohydrate-benzene complex lead us to idea about possible additivity of the CH-π interaction. Therefore, E_{int} of bidentate carbohydrate-napthalene complexes were analyzed. The hypothesis of total additivity of the interaction was not confirmed. However, the E_{int} exhibits certain degree of additivity. The E_{int} of bidentate complex forms 2/3 of sum of E_{int} of monodentate ones and 4/5 of sum of E_{int} of carbohydrate-benzene complexes.

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Keywords: *carbohydrate; benzene; naphtalene; ab initio calculations; density functional calculations;*

P-0027

DEPROTONATED G8 AND PROTONATED A38 IN THE GENERAL ACID/BASE MECHANISM OF THE HAIRPIN RIBOZYME SELF-CLEAVAGE REACTION PATHWAY

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The hairpin ribozyme is a member of the group of small ribozymes, performing self-cleavage and -ligation without direct participation of metal ions. Experiments identified two catalytically active residues, guanine 8 (G8) and adenine 38 (A38), but their exact roles remain still elusive. We carried out all-atom molecular dynamics (MD) simulations in explicit solvent on 50-500 ns time scales in order to compare the impact of various protonation states of G8 and A38. We observed that the geometries with the canonical G8 and protonated $A38H^+$ agreed well with the crystal structures, while those bearing a deprotonated $G8^-$ and a canonical A38 gradually perturbed the active site. The geometries generated by MD simulations were further analyzed by the hybrid quantum-mechanical/molecular mechanical (QM/MM) method. We calculated energies along the reaction pathways and indentified activation barriers and rate-limiting steps. We found three possible reaction scenarios with activation barriers in good agreement with those derived from experiment (20-21 kcal/mol). These scenario were: (**i**) a general base (deprotonated $G8^-$)/general acid (protonated $A38H^+$) mechanism with activation barrier of 20.4 kcal/mol; (**ii**) two mechanisms involving a proton shuttle via the nonbridging oxygen in the presence of canonical G8 together with either A38 or $A38H^+$ (20.5 or 21.0 kcal/mol, respectively); and (**iii**) a combined proton shuttle/general acid mechanism with canonical G8 and protonated $A38H^+$ (21.0 kcal/mol). In all cases, the initial nucleophile attack of the A-1(2'-OH) group on the scissile phosphate represented the rate-limiting step along the reaction path. We suggest that RNA self-cleavage may benefit from several microscopic pathways that are energetically comparable. Among those pathways, the reaction mechanism with deprotonated $G8^-$ as general base and protonated $A38H^+$ as general acid is the most consistent with the experimentally measured kinetic pH profiles.

Keywords: *Enzyme catalysis; Ribozymes; Cleavage reactions;*

P-0028

ADSORPTION OF HCN ON LEWIS SITES OF MICROCRYSTALLINE GAMMA-ALUMINA: A QUANTUM CHEMICAL CLUSTER MODEL STUDY

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Adsorption of HCN on the surface-exposed acidic Lewis sites of microcrystalline γ-alumina was studied by a quantum chemical cluster model approach, with an emphasis on the potential usage of HCN as a test-probe molecular system. B3LYP/6-31++G(*d*,*p*) and HF/6-31++G(*d*,*p*) levels of theory were employed, considering the standard and counterpoise-corrected potential energy surfaces (PESs) of HCN attached to finite clusters modeling the surface. The main focus was put on the non-polar (100) and (110) crystal planes of microcrystalline γ-alumina. Neutral cluster models representing the non-polar (100) and (110) planes were derived from the crystal structure of γ-Al_2O_3. Termination of the clusters at the bulk-cluster interfaces was performed by OH groups or HOH molecules. Both the standard and the counterpoise-corrected potential energy surfaces of free HCN, as well as of HCN-$Al(OH)_x(H_2O)_y$ clusters in the ground electronic state were explored at the above-mentioned levels of theory. Explicit inclusion of dynamical electron correlation effects and the elimination of the basis set superposition effects in geometry optimization was found to be significant factor in order to reproduce the experimental trends in the shifts of the HCN C-H stretching mode frequencies upon adsorption. Both harmonic and anharmonic vibrational analyses of the HCN C-H stretching motion were performed. The later were based on sequential computation of the C-H stretching vibrational potentials for the free and adsorbed HCN molecule (on various clusters) and solution of the corresponding vibrational Schrodinger equation by the variational method. Bader and NBO analyses of the electronic density were employed in order to make a proper classification of the type of intermolecular interaction (covalent versus noncovalent) in the course of HCN adsorption on microcrystalline γ-alumina.

Keywords: *HCN; adsorption; Lewis adsorption sites; gamma-alumina (?-Al2O3);*

P-0029

METAL-ORGANIC MOLECULAR UNITS FOR INDUCED STRUCTURE MANIPULATION

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Interfaces between metal atoms and organic molecules are key units of metal-organic frameworks, connections between metal electrodes and molecular “wires”, catalysis-related species. A large class of such interfaces is represented by sandwich-type complexes with the molecules on both sides of the atoms. Most of such systems involve transition metals, while main-group light metals may induce features related to closer proximity of the molecules combined with their favourable orientation [*Chem.Phys.Lett*. 499 (2010) 203].

Presented are results of ab initio calculations for a series of complexes of light-metal atoms sandwiched between small unsaturated hydrocarbon molecules. Evolution of the system structure and stability is systematically studied for different metal atoms, as well as upon ionization and electron attachment. Predicted interesting features include non-additive stabilization on adding second molecule to the half-sandwich precursor, unusual geometries in some cases, and reversible charge- or excitation-governed geometry alterations. The latter variations are found to reflect structure similarities for isoelectronic systems. Such properties apparently suggest potential applications of the above species as stable intermolecular junctions and units with charge- or spin-controlled shapes in molecular devices and/or machines.

Additional point of interest is the metal-atom induced fusion of the sandwiching molecules, leading to another isomer of the system. Different metals are predicted to favour different isomers, with such catalysis producing higher-energy species in some cases. Stability towards detachment of the metal atom from the fused molecular species (thus completing the catalytic cycle) is addressed.

Also considered is a system of one or two metal atoms and a single larger molecule with a few suitably positioned unsaturated fragments. It is found to exhibit similar, although intra-molecular, nonadditive stabilization and metal-atom induced isomerization. Mutual influence of metal-attachment sites and their effect on the isomerization are analyzed as well.

Keywords: *Ab initio calculations; Sandwich complexes; Main group elements; Isomers; Molecular devices;*

P-0030

CONFORMATIONAL STUDIES OF BETA-PEPTIDES THROUGH THE USE OF LMP2-COSMO AND MOLECULAR DYNAMICS

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The study of β-peptides secondary structures has gained substantial interest over the last years. Compared to α-peptides, the additional carbon in their backbone provides an extra degree of freedom due to the added torsional angle. This feature allows β-peptides to adopt a large number of distinct secondary structures with relatively low energy differences.

β-peptides seem to have an intrinsic tendency to fold into periodic structures, although the nature and relation of these interactions are not quite well understood. This appears to be related with local torsional angles as well as backbone-side chain and side chain-side chain interactions.[1] The use of local correlation methods with implicit solvent model have shown to be promising method to describe the properties of hexamers of such systems.[2]

In an attempt to characterize and better understand the β-peptides conformational landscape, several oligopeptide geometries were optimized with DFT methods in different polarity environments. The energetics were then refined through single point energy calculations carried out at the level of local second order Müller Plesset perturbation theory (LMP2)[3] in combination with the COSMO model.[4] Density-fitting approximations, which reduce the computational cost relative to the basis set size, were also applied. Molecular dynamics simulations were also carried out in order to treat the solvent explicitly and complement the quantum mechanics studies.

The results underline the applicability local correlated methods in the characterization of such systems, as well as the influence of the side chain groups.

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Keywords: *Peptides; Molecular dynamics; Ab initio calculations;*

P-0031

QSPR MODELLING OF LIPOPHILICITY AND ANTITUBERCULAR ACTIVITY OF THIOBENZANILIDE DERIVATIVES

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The search for novel drugs against bacterial infections like tuberculosis, a disease caused by *Mycobacterium tuberculosis* (*M. tb*) and other mycobacterioses, is one of the goals of present-day pharmaceutical industry, given the enormous impact of these pathologies on public health worldwide[1] and, in the case of *M. tb,* also due to the alarming spread of multi-drug resistance reported cases. Thiobenzanilides, which are relatively weakly toxic to higher organisms, have been found to show strong biological activity as anti-tubercular agents.

In this work we have analyzed a large set of thiobenzanilide derivatives (189 compounds), taken from literature, and have derived two quantitative structure-properties relationships (QSPRs) relating the lipophilicity, measured as clog*P*, and the anti-tubercular activity, measured as log(1/*MIC*), of these compounds with various computed molecular descriptors. QSPR models were generated by multiple linear regressions (MLR) using a forward stepwise variable selection.[2] The database was divided into a training set and an independent test set with similar variability. The best descriptors related to either lipophilicity (clog*P*) or biological activity (*MIC*) were selected on the basis of rigorous statistical criteria. The obtained model equations were internally and externally validated, in order to assess the robustness and predictive ability of the developed QSPR models. The best found equations showed a good interpretative ability and an effective predictive power towards test set compounds and will be used to assist us in the rational design and synthesis of new active thiobenzanilide derivatives.

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Keywords: *thiobenzanilides; anti-tubercular activity; lipophilicity; quantitative structure-property relationship;*

P-0032

INTERACTIONS BETWEEN SELECTED BILE SALTS AND TRITON X-100 OR SODIUM LAURYL ETHER SULFATE

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Background: In order to develop colloidal drug carriers with desired properties, it is important to determine physico-chemical characteristics of these systems. Bile salt mixed micelles are extensively studied as novel drug delivery systems. The objective of the present investigation is to develop and characterize mixed micelles of nonionic (Triton X-100) or anionic (sodium lauryl ether sulfate) surfactant having oxyethylene groups in the polar head and following bile salts: cholate, deoxycholate and 7-oxodeoxycholate.

Results: The micellization behaviour of binary anionic-nonionic and anionic-anionic surfactant mixtures was investigated by conductivity and surface tension measurements. The results of the study have been analyzed using Clint’s, Rubingh’s, and Motomura’s theories for mixed binary systems. The negative values of the interaction parameter indicate synergism between micelle building units. It was noticed that Triton X-100 and sodium lauryl ether sulfate generate the weakest synergistic interactions with sodium deoxycholate, while 7-oxodeoxycholate creates the strongest attractive interaction with investigated co-surfactants.

Conclusion: It was concluded that increased synergistic interactions can be attributed to the larger number of hydrophilic groups at a side of the bile salts. Additionally, 7-oxo group of 7-oxodeoxycholate enhance attractive interactions with selected co-surfactants more than 7-hydroxyl group of sodium cholate.

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Keywords: *Micelles; Molecular recognition;*

P-0033

INTERACTIONS BETWEEN SODIUM CHOLATE OR SODIUM DEOXYCHOLATE AND NONIONIC SURFACTANT (TWEEN 20 OR TWEEN 60) IN AQUEOUS SOLUTION

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Knowledge of physicochemical parameters of mixed micelles is important in order to develop drug delivery systems with required characteristics. Investigated bile salts and Tweens are relatively nontoxic surfactants, extensively studied as biocompatible colloidal drug carriers. The micellization behavior of binary anionic-nonionic surfactant mixtures built of sodium cholate or sodium deoxycholate and one of two Tweens (Tween 20 or Tween 60) was investigated by conductivity and surface tension measurements. The results of the study have been analyzed using Clint’s, Rubingh’s, and Motomura’s theories for mixed binary systems. The determined physicochemical properties, particularly the negative values of the interaction parameter, indicate synergism between the individual surfactants in the mixed micelles. It was noticed that Tween with a longer hydrophobic tail shows stronger interactions with selected bile salts. However, it was found that the more hydrophilic bile salt (sodium cholate) generates the stronger synergism with investigated Tweens.

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Keywords: *bile acids; mixed micelle; Tween;*

P-0034

INTERACTION OF SMALL RNA MOLECULES WITH GRAPHENE SURFACE

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Hairpins belong to the most important structural motifs in RNA. Many of them play key roles in relevant biological processes such RNA-folding and interactions that determine the tertiary structure of RNA molecules. In combination with graphene, RNA fragments may become interesting in many applications, for instance in sensing, similarly as DNA. But in comparison to DNA, little is known about RNA-graphene interactions to date. In this work we focused on the GAGA tetraloop, which is found in sarcin-ricin loop in ribosome, where it serves as a recognition site for some ribotoxins. We carried out molecular dynamics simulations of this tetraloop in water and also at the graphene-water interface. We used various techniques such as potential of mean force (PMF) or targeted MD to investigate the influence of graphene on the stability of these motifs.

Keywords: *Molecular dynamics; Graphene; RNA; Biosensors;*

P-0035

LOCAL SPIN: IMPROVED HILBERT-SPACE ANALYSIS

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The local spin is a key concept for the characterization of magnetic properties of transition metal complexes and clusters, and also for establishing the radical character of molecules or reactive processes. In recent years there has been an increasing interest in recovering local spins from ab initio wavefunctions.[1–6]

We have shown[6] that there is actually a continuum of different formulations that fulfill all physical requirements imposed to date to the decomposition of s^2, and this applies to both single- and multideterminant wave functions. In order to find the best local-spin decomposition scheme, we impose a new, additional requirement related to the one-electron distribution that eliminates the ambiguity. The resulting local-spin decomposition is thus unique and fulfills all physical requirements found so far. Moreover, there is an apparent ambiguity in decomposing two-electron quantities in the framework of Hilbert-space analysis that, to date, has not received due attention. This problem is particularly relevant in the case of the decomposition of s^2 The numerical implementation has been carried out in the Hilbert-space. A series of representative closed-shell and open-shell systems have been used to illustrate the performance of this new decomposition scheme against other existing approaches. Unlike other decompositions of s^2, the new scheme provides very small local-spin values for genuine diamagnetic molecules treated with correlated wave functions.

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Keywords: *ab initio calculations; quantum chemistry;*

P-0036

COHERENT EXCITATION OF NEON IN THE EXTREME ULTRAVIOLET REGIME

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Coherent excitation of atomic transitions is a general phenomenon that may result in coherent transients. These are a signature of interferences between resonant and non-resonant excitation pathways. This fundamental process has been investigated using ultrashort laser pulses in the near infrared regime[1]. An extension of the investigation of these fundamental processes from the optical to the extreme ultraviolet (xuv) regime has become feasible with the development of ultrashort xuv light sources. High-order harmonic generation is a well-established technique for producing ultrashort radiation in the xuv range.

In this work we investigate the coherent excitation of a superposition of Rydberg states in neon by the 13th harmonic of an intense 804 nm pulse and the formation of a wave packet[2]. We present pump-probe experiments performed on the 3d manifold of neon where the $2p^6$ $2p^5$ $(^2P_{3/2})$ 3d [1/2] and $2p^6$ $2p^5(^2P_{3/2})$ 3d [3/2] transitions are excited at 20.04 eV photon energy. The temporal evolution of the excited wave packet is probed by ionization with a time-delayed 804 nm pulse. We demonstrate the control of the coherent transient excitation of neon and the wave packet dynamics in the xuv regime using the spectral phase of the 13th harmonic as a control parameter, where the modulation of the phase is achieved by propagation of the xuv pulse through a variable optical density of neon gas. The experimental results indicate the possibility to control fundamental coherent excitation processes in the xuv regime using phase-shaped high-order harmonics.

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Keywords: *Time-resolved spectroscopy; Photoelectron spectroscopy;*

P-0037

ROLE OF EXONS IN STABILIZATION OF PROTEIN STRUCTURE

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The role of exons can be interpreted on many aspects. One of them is the relation of exons to the 3-D structure of protein. It has been shown that fragments of the secondary structural forms are not accordant with sequence fragments accordant with exons.

The relation between exon fragments and their structural status in 3-D structural forms is under consideration. Particularly the relation between tertiary structure of the protein and the structure of exons present in particular protein has been analyzed. The stabilization of tertiary structure is estimated on the basis of hydrophobic core structure. The participation of exons in hydrophobic stabilization is measured to reveal the role of each exon-fragment.

The exons in selected proteins (100) were identified on the basis of information in GenBank files taken from nucleotide database in National Center of Biotechnology Information. The amino acid sequence representing particular exon was identified. The defined sequence fragments were localized in 3-D structural forms of proteins (PDB).

The participation of each exon-fragment in the construction of hydrophobic core was measured using the divergence entropy calculation showing their differentiate role in the stabilization of tertiary structure.

It was revealed that the presence of at least one exon, of which the structure of polypeptide fragment is accordant with expected ordered structure of hydrophobic core. It means that the probable role of at least one exon is to generate the hydrophobic core responsible for tertiary stabilization in proteins.

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Keywords: *exons; hydrophobic core; divergence entropy;*

P-0038

CALCULATION OF FRANCK-CONDON FACTOR FOR HARMONIC OSCILLATORS

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A formula of Franck-Condon factor for harmonic oscillators has been derived from reference. The formula will be used as an implementation for calculating rate of electron transfer. Also, the applications of Franck-Condon factor have been conducted by comparing with DFT calculation of S_2O molecule with various basis sets.

Keywords: *Franck-Condon factor; harmonic oscillator;*

P-0039

LIGHT-DRIVEN-COORDINATION INDUCED SPIN-STATE SWITCH: RATIONAL DESIGN OF PHOTODISSOCIABLE LIGANDS USING DENSITY FUNCTIONAL THEORY METHODS

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The coordination of axial ligands to porphyrins is of fundamental importance in many areas of chemistry, biology and material science.[1] Azopyridinederivates which are isomerizing between the cis and trans configuration upon irradiation with UV and visible light were used to realize a Light-Driven-Coordination Induced Spin-State Switch (LD-CISSS) at Ni(II)-porphyrins.[2,3] Upon the association/dissociation of axial ligands the Ni(II) center can be switched between the high spin (HS) and the low spin (LS) state. Whereas the trans isomer binds with its pyridine nitrogen the coordination of the bent cis isomer is sterically hindered. We performed density functional theory calculations to find a substitution pattern at the phenylazopyridine ligand which provided an optimum switching efficiency. A similar approach with the photochromic ligands covalently attached to the porphyrin has recently been published.[4]

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Keywords: *Computational chemistry; Quantum Chemistry;*

P-0040

SERINE-BASED SURFACTANTS AS PROMISING CARRIERS FOR GENE DELIVERY: DNA COMPACTION STUDIES WITH SINGLE-SURFACTANT AND CATANIONIC LIPOSOMES

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Cationic lipoplexes have emerged as a potential alternative to viral vector-mediated gene delivery for *in vitro* and *in vivo* applications. Liposomes formed by phospholipids may show problems of chemical stability, as these molecules can easily undergo chemical degradation by hydrolysis and peroxidation. Furthermore, these liposome formulations are frequently non-spontaneous and non-equilibrium structures, with limited colloidal stability in time. Such shortcomings may compromise, in turn, the formation, stability and efficiency of lipoplexes. The use of amino acids for the synthesis of surfactants with liposome-forming properties provides the route for novel biofriendly liposomes that can aim at DNA compaction. These liposomes that either be based on single surfactant systems or in catanionic mixtures, in the latter case with enhanced chemical/colloidal stability and the possibility of charge manipulation[1].

In this context, we have been involved in the synthesis and evaluation of the self-aggregation properties of a variety of ionic amino acid-based surfactants. On the basis of previous screening toxicological studies, our efforts have been directed towards serine-based surfactants[2]. Here, we report the study of the phase behavior and microstructure of some serine-based catanionic mixtures composed by monomeric single-chained cationic (C12, C16) and monomeric double-chained anionic (C8-8, C12-12) surfactants. The phase diagrams of two serine-based cationic gemini surfactants, $(12Ser)_2CON12$ and $(12Ser)_2COO12$, which spontaneously form vesicles, are also presented. The synthesis of the compounds has been performed according to a methodology established in our laboratory. The mixtures have been characterized by differential scanning calorimetry, video-enhanced light microscopy and cryo-scanning electron microscopy. DNA compaction studies have been also performed, by means of fluorescence microscopy.

Acknowledgement: *Thanks are due to FCT (PTDC/QUI/115212/2009; SFRH/BD/61193/2009; CIQUP)*

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Keywords: *Amino acids; Surfactants; Vesicles; DNA;*

P-0041

HYBRID QM/QM APPROACHES USING LOCAL EXPLICITLY CORRELATED METHODS

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Notwithstanding the popularity of DFT, wave function methods remain a standard for highly accurate computational chemistry studies. However, accuracy comes at a high price in the form of long computation times for even a few atoms and a decent basis set. To get around this inherent problem, methods such as QM/MM and local correlation methods have been introduced.[1] The former places the emphasis on a certain area of a complex structure, in which most of the change occurs, while the latter makes use of the fact that correlation is actually a short range effect. Both methods enable the study of much larger systems, but possess their own faults. QM/MM approaches may require large QM regions to avoid artifacts in their interaction with the environment. Local coupled cluster methods, even if low-order scaling, may still be too costly for routine applications. A solution to these problems is a hybrid QM/QM approach where the whole molecule is treated quantum mechanically. The system is divided into a region of interest and an outer region, computed at a lower level. Through the use of local orbital spaces,[2] no bonds have to be broken.

In this work we apply hybrid QM/QM approaches with local explicitly correlated methods, i.e. LMP2-F12 and LCCSD(T0)-F12,[3] to calculate reaction energies and barriers of different reaction types (e.g. peptide bond formations). This method was also used to calculate barriers for an enzyme catalized reaction with coupling to MM.[4] Calculations with different region sizes support the efficiency of this approach and further test systems are suggested.

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Keywords: *Ab initio calculations; Computational chemistry; Peptides;*

P-0042

APPLICABILITY OF MARCUS THEORY IN IONIC LIQUIDS. EVIDENCE FROM ESR LINE BROADENING EXPERIMENTS

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For more than half a century Marcus Theory[1] has been one of the cornerstones in the understanding of outer-sphere electron transfer reactions. The theory, together with many further developments[2,3], provides a thorough theoretical description of the reaction energetics and kinetics and has been substantiated by numerous experimental findings. Since Marcus Theory was developed for polar liquids, using a dielectric continuum approach, it is interesting to know to what extent it can be applied to electron transfer in ionic liquids.

In the past, ESR line broadening experiments[4] on electron self-exchange reactions in polar solvents have provided a wealth of experimental information on Marcus Theory and thus suggest themselves for similar studies in ionic liquids.

Several well-known self-exchange systems[5,6] have been investigated in some common imidazolium based ionic liquids using ESR spectroscopy at room temperature and at variable temperatures or pressures. The experimental results, such as rate constants, reorganization energies or solvent dynamic effects are compared to their analogues from traditional solvents, as well as to existing findings from literature, obtained using other experimental methods.

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Keywords: *ESR; Electron Transfer; Ionic Liquids;*

P-0043

TERMINATION MECHANISMS FOR POLYOLEFIN LIVING CATALYSIS AT DFT LEVEL

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Living polymerization is a hot topic in post-metallocene catalysis.[1, 3] In fact, the synthesis of ultra-high molecular weight polyethylene and block copolymers and the understanding of the reaction mechanisms of the termination step are still challenging.

Fujita *et al.*[1] have been the first to highlight the living behaviour of bis(phenoxyimine)Ti catalysts in the polymerization of ethylene and propylene.

Mecking *et al.*[2] showed that the new bis(enolatoimine) Ti catalyst, with *ortho*-fluorinated aryl groups, is able to achieve the same living behaviour. Via NMR, the key role of the F-bond interactions *o*-F···Ti in the suppression of the H_β-termination was proposed.

In this communication, we investigate the mechanism of the H_β-transfer in the termination reaction. The models used are Mecking's catalysts. DFT calculations were performed on a parallel platform using GAUSSIAN09.

A procedure to simulate the termination reaction, usually based on forcing the cleavage of Ti-C_α bond, has been developed. The stationary structures have been localized and energy barriers of activation determined. In transition states' calculations, normal mode analysis has been performed. The protective role of the fluorine *o*-F···H and *o*-F···Ti bonds in the reactive species, and repulsive *o*-F···*o*-F interactions destabilizing the transition states, have been unraveled. An alternative H_β-transfer to the ligand, with formation of an alkoxyimine, in the termination mechanism of *ortho*-hydrogenated or -methylated non-living catalysts is proposed.

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Keywords: *Hydrogen transfer; Density functional calculations; Fluorinated ligands; Polymerization; Reaction mechanisms;*

P-0044

EFFECT OF ETHYNYL AND THIOPHENE-2-YL SUBSTITUENTS ON COMPLEXATION OF 4'-SUBSTITUTED 2,2';6',2"-TERPYRIDINES WITH ZN^{2+} AND FE^{2+} IONS AND SPECTROSCOPICPROPERTIES OF FORMED COMPLEXES.

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Metallo-supramolecular polymers are macromolecules composed of defined oligomeric molecules with chelate end-groups, which are linked to chains through reversible coordination to metal ions. Strength of this interaction depends on choice of ligand as well as metal ions.

Appropriate combination of metal and ligand is the key to obtain polymer with demanding properties.

2,2':6',2"-Terpyridine is easy to functionalized and can be used as chelate end-groups for oligomeric components of electromagnetic-field-responsive metallo-supramolecular polymers

for photovoltaic applications. Iron (II) and zinc (II) ions are typical ions used in metallosupramolecular polymers composed of terpyridine capped π-conjugated oligomers.

Terpyridine end-groups can be linked to molecules of various conjugated oligomers via ethynediyl or thiophene-2,5-diyl moieties. As these moieties can significantly influence their properties, knowledge of them is of high interest since it allows discriminating contributions of the oligomeric chains to the properties of resulting metallo-supramolecular polymers.

Therefore, we thoroughly studied complexation of 4'-ethynyl- and 4'-(thiophene-2-yl)-terpyridine with Zn^{2+} and Fe^{2+} ions using the UV/vis, NMR and fluorescence spectroscopy in order to (**i**) determine stability constants of complexes formed, (**ii**) obtain an insight into the spectral changes accompanying these complexations. In addition, we measured stability constants and examined spectral properties of Zn^{2+} and Fe^{2+} complexes of unsubstituted terpyridine in order to get a solid basis for the evaluation of the substituent effects.

The obtained results show that stepwise addition of Zn^{2+} ions to ligand (L) solution, gives as first species $[ZnL_2]^{2+}$ and then $[ZnL]^{2+}$ in proportions depending on the Zn/L molar ratio. In

contrast, added Fe^{2+} ions give exclusively species $[FeL_2]^{2+}$ that, according to UV-VIS and NMR spectra do not undergo transformation into $[FeL]^{2+}$.

Stability constants of forming complex ML and ML_2 were calculated. All complexes were found to be stable under applied conditions.

Keywords: *UV/Vis spectroscopy; NMR spectroscopy; Supramolecular chemistry; N ligands;*

P-0045

CLUSTER FORMATION IN SOLVATED BISMUTH COMPLEXES

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Our research is focusing on the formation of clusters in solvated metal systems, in this case mixed bismuth hydroxide and bismuth nitrate clusters in Dimethylsulfoxide, and nucleation and phase change in these systems. The objective is to characterize mechanisms by which such phase changes occur and the associated parameters which promote the phase change best.

Our side of this research project centers on computational methods, namely molecular dynamics and statistical analysis, using the DL POLY package and the OPLS force field, through which both properties in solution and after beginning nucleation are assessed and quantized for dynamic and thermodynamic properties. The next step will be to calculate exchange energies of bimut octahedra in different ion caged (OH^-, NO_3^-, $(OH^-)_x(NO_3^-)_y$) and with added ions (Na^+ OH^-) in solution. After this assessment and parameterization the Kawska-Zahn-Method of simulating nucleation is used to speed up the process, enabling more detailed studies of the nucleation.

Thus far an inherent stability in octahedral clusters of the type $(Bi_6(NO_3)_6(OH)_4O_4)_x(DMSO)_y$ has been revealed, necessitating modification of the anion cage in which the bismuth ions are embedded. Associated NO_3^--ions show some degree of a tendency to migrate inside the solution and between bismuth octahedra, giving the octahedra a net charge, while OH^- and O^{2-}-ions are stably bound.

This research is part of the DFG SPP 1415 grant programme, "Crystalline Non-equilibrium phases – Preparation, characterization and in-situ examination of formation mechanisms"

Keywords: *Bismuth; Molecular Dynamics; Phase transitions; Cluster compounds;*

P-0046

FLUOROPHORS FOR INVESTIGATING ORGANIC REACTIONS ON THE SINGLE MOLECULE LEVEL

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The knowledge of organic reaction mechanisms is of utmost relevance in synthetic chemistry. Optimization requires a deep insight into the mechanisms. A convenient way to determine the individual steps of the transformation can be accomplished by single molecule experiments. We designed two systems, one for studying the epoxidation and the other for studying the metathesis reaction by means of fluorescence spectroscopy. The class of Borondipyrromethene (Bodipy) dyes is used as fluorophor scaffold because of their adequate qualities for single molecule experiments, i.e. a high fluorescence quantum yield and a high photostability[1]. Furthermore, the Bodipy dyes exhibit a neutral, apolar chromophore which is easily accessible and modifiable[2,3]. Prolongation of the chromophoric unit by a chemical reaction leads to an orange fluorescent dye[4].

As a first example, we visualize the epoxidation of a double bond via m-Chloroperoxybenzoic acid (MCPBA). The Bodipy is immobilized on a surface and the reaction is detected via TIRF-microscopy by a blueshift of the emission-wavelength[5].

Currently we investigate the metathesis reaction. We synthesized an immobilized metathesis catalyst which reacts with a vinyl-Bodipy dye. Here, the transformation of the vinyl- to a styryl-compound is seen in the bathochrome shift of the fluorescence wavelength. Recent results are discussed at our presentation.

With the current approach, our long-term goal of mapping complex potential energy surfaces comes into reach[6].

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Keywords: *single-molecule studies; Metathesis; Fluorescent probes; Reaction mechanisms; Ruthenium;*

P-0047

GLASS-FORMING TENDENCY OF THE BINARY SYSTEM WATER + OXYETHYLATED GLYCEROL (N=25)

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In this study relation between low temperature phase behavior and intermolecular interactions in a system low-molecular polymer+water is discussed. At the present time aqueous solutions of oxyethylated glycerol of different polymerization degree are suggested to be used as components of cryoprotective media for low temperature preservation of biological objects. One of criteria of efficiency of a cryoprotectant is its ability to prevent formation of ice causing damage and death of biological cells. Therefore study of phase behaviour and glass-forming tendency of cryoprotectant-containing aqueous solutions is of immediate practical importance. It is known that compounds forming intermolecular hydrogen bonds have a strong glass-forming tendency. In the present work, physical states of the binary system water+oxyethylated glycerol of polymerization degree n=25 (OEGn=25) were studied below 273 K over all the concentration range by DSC and optical cryomicroscopy. The hydration number characterizing intermolecular interactions was determined on the basis of DSC and IR-spectroscopy data. The phase diagram of the water–OEGn=25 system was plotted. It has been found from the diagram and the optical cryomicroscopy results that ice crystallization occurs and concentrated unfrozen residues remain during cooling at low OEGn=25 concentrations. The system hardens in the amorphous state during cooling and ice crystallization occurs during heating at medium concentrations. Crystallization is observed neither during cooling nor the subsequent heating at moderately high concentrations. OEGn=25 crystallization occurs at high concentrations. According to the phase diagram analysis, each OEGn=25 molecule can bind about 72 water molecules and about 36 of them are strongly bound. The hydration number of OEGn=25 is found to be about 75 by IR-spectroscopy. Thus the binary system water+OEGn=25 has sufficiently high glass-forming tendency due to containing a large number of polar groups able to form numerous hydrogen bonds with water.

Keywords: *Hydrogen bonds; Polymers; Glasses; Phase transitions; Phase diagrams;*

P-1016

APPARENT OR REAL WATER EXCHANGE REACTIONS ON $[ZN(H_2O)_4(L)]^{2}+ 2H_2O$

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The exchange of a second coordination sphere water molecule in $[Zn(H_2O)_4(L)]^{2}+\cdot 2H_2O$ (L = N-donor Ligand)[1-3] against a coordinated water molecule in the first coordination sphere was studied by quantum chemical calculations (RB3LYP/6-311+G**). The complete reaction consists of an associative binding of one H_2O from the second coordination sphere leading to a six-coordinate intermediate, followed by the dissociation of a water molecule to reach the product state $[Zn(H_2O)_4(L)]^{2}+\cdot 2H_2O$. For a real water exchange reaction to occur two different transition states have to be included, otherwise only an apparent water exchange reaction takes place. For the water exchange reaction in $[Zn(H_2O)_4(L)]^{2}+\cdot 2H_2O$ nearly iso-energetic cis- and trans-orientated transition states are crossed. The basicity (described as the gas-phase proton affinity) of L shows instructive correlations with structural parameters and energy gaps for the investigated reactions.

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Keywords: *Calculated water exchange reactions;*

P-0048

CYTOTOXICITY OF NEW THIADIAZOLO[2,3-A]PYRIDINE BENZAMIDE DERIVATIVES ON FIVE CANCER CELL LINES

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Cancer is a serious clinical problem which can develop in almost any organ or tissue, but they are classified by the type of cell that is initially affected such as the skin, bone, lung, colon, breast and nerve cancer.

There are some therapy options like surgery, chemotherapy, endocrine and radiation therapy in the treatment of cancer. Chemotherapy is an important treatment for cancers. However, toxicity and poor tolerance to current chemotherapeutic agents are dose-limiting factors. Therefore, discovery and development of apoptosis inducers as new chemotherapeutic agents is a promising approach.[1]

In this study, three derivatives of Thiadiazolo[2,3-a]Pyridine Benzamide were synthesized in two steps. First step, reaction between three derivatives of 2-aminopyridine and benzoylisothiocyanate formed three thiourea derivatives; **a**) N-Benzoyl-N-(2-Pyridyl)Thiourea (PyTuBenzo), **b**) N-Benzoyl--N-(4-Methyl-2-Pridyl)Thiourea (4PicTuBenzo) and **c**) N-Benzoyl--N-(6-Methyl-2-Pyridyl)Thiourea (6PicTuBenzo). Second step, three thiourea derivatives were oxidized by Cu^{2+}. The oxidized products were Thiadiazolo[2,3-a]Pyridine Benzamide derivatives as a second group; **a`**) N`-(2H-[1,2,4]-Thiadiazolo[2,3-a]Pyridine--2-Ylidne)Benzamide (2HThPyBenza), **b`**) N`-(7-Methyl--2H-[1,2,4]Thiadiazolo[2,3-a]Pyridine-2-Ylidne)Benzamide (7MeThPyBenza) and **3`**)N`-(5-Methyl-2H-[1,2,4]Thiadiazolo[2,3--a]Pyridine-2-Ylidne)Benzamide (5MeThPyBenza). The products in two steps were characterized by FTIR, ^{1}HNMR and ^{13}CNMR spectroscopies and their crystal structures were determined.

In vitro cytotoxic activity of the six products were studied by five human cell lines include Breast cancer cell line MDA-MB-231, Prostate adenocarcinoma cell line LNCap, Neuroblastoma cell line SK-N-MC, Nasopharyngeal epidermoid carcinoma cell line KB and Liver cancer cell line HEPG-2. The results were compared with Doxorubicin using MTT-dye reduction assay.

In vitro results suggested that the second group inhibited the growth of cancer cell lines. Among these Benzamide derivatives in this group, 7MeThPyBenza showed the best results for four human cell lines than the other derivatives.

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Keywords: *Thiadiazolo Benzamide; Cytotoxicity; Cancer cell line; [2,3-a]Pyridine Benzamide;*

P-0049

TARIQUIDAR-RELATED MODULATORS OF ABC TRANSPORTERS PREFERRING THE BREAST CANCER RESISTANCE PROTEIN (ABCG2)

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ABC inhibitors have been developed to overcome multidrug resistance and to reach tissues that express ABC efflux transporters.

Aiming at structural optimization of potent and selective ABCG2 inhibitors, such as UR-ME22-1, from our laboratory, an efficient solid phase synthesis was developed to get convenient access to this class of compounds.

The inhibition of ABCB1 and ABCG2 was determined in the calcein-AM and the Hoechst 33342 microplate assay, respectively. Compounds bearing triethylene-glycol ether groups at the tetrahydroisoquinoline moiety were more efficient in the testing, due to increased solubility in water.

The stability of the ABCG2 inhibitors in serum, which is crucial for cell culture testing and even more for *in vivo* experiments, was determined by incubation with serum and HPLC measurements. Unfortunately, the amide bond of the potent ABCG2 inhibitor UR-ME22-1 was rapidly cleaved. Therefore, new generations of inhibitors with higher stability against enzymatic cleavage are under development. Early results are promising for a new series of compounds.

Keywords: *solid phase; abcg2; breast cancer resistance protein; stability;*

P-0050

ASCORBATE PEROXIDASE ACTIVITY WITH CYTOCHROME C

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Cytochrome c, a metalloprotein of the electron transport chain, is also known to be involved in apoptosis, most probably due to its free radical reactivity, and in particular interaction with peroxide. Under conditions where the sixth coordination position at the cytochrome c heme iron become more accessible for exogenous ligands (including changes in pH or temperature), this peroxidase activity is enhanced. Here, it is shown that treatments favoring liberation of the sixth coordination position at the cytochrome c heme iron and therefore increased accessibility for peroxide (by partial denaturation with guanidinium hydrochloride) lead to a drastic increase in the reactivity of cytochrome c towards hydrogen peroxide, to the point where the ascorbate peroxidase activity demonstrated here for native cytochrome c is drastically improved (both in terms of Km and Vmax). Moreover, a reaction intermediate is detected by stopped-flow UV-vis spectroscopy upon treatment of guanidine-treated cytochrome c with peroxide, which resembles the spectrum of globin Compound II and is thus proposed to be a high-valent ferryl species – the first of its kind to be directly detected in a cytochrome c at room temperature. The ability of physiological levels of ascorbate (10-60 μM) to interact with this species may have implications for mechanism of cell signaling or damage that are based on cytochrome c/peroxide interactions. Electron paramagnetic resonance (EPR) data support these findings.

Keywords: *cytochrome c; peroxide; ascorbate;*

P-0051

COMPLEMENT PROTEIN C-REACTIVE PROTEIN BINDING TO CURVED SUPPORTED LIPID BILAYERS

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This project is advancing research into cardiovascular disease by investigating C-reactive protein's (CRP) interaction with curved membrane surfaces, a condition present in apoptotic cells found in inflamed tissue of atherosclerotic plaque. By using nanoparticles of varying diameters, we have induced curvature in a phospholipid bilayer independent of other factors typically present in a biological system (such as oxidized lipid). Nanoparticles were deposited onto a glass substrate prior to creation of a supported lipid bilayer (SLB), which induces curvature in the bilayer as it forms. Liposomes are suspended in solution via sonication, settle onto glass, and form bilayer sheets. Using confocal microscopy, SLB fluidity has been observed and diffusion rates characterized for bilayers formed over differently sized nanoparticles. We have used two different diameter nanoparticles: 40 nm and 100 nm. No significant differences were seen for flat bilayers compared to patterned bilayers. Curvature specific binding has also been observed for native and modified forms of CRP to these patterned SLBs. After modification, localization of CRP to curvature increased significantly. Higher extents of curvature (lower radius particles) showed a greater change in binding to higher colocalization percentages than those of lower extents of curvature.

Keywords: *Membranes; Biophysics; Nanostructures; Proteins;*

P-0052

SCLEROTINIA SCLEROTIORUM LACCASE PRODUCTION. INSIGHTS INTO THE PHYSIOLOGICAL ROLE

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Laccases are multicopper oxidases that catalyze the one-electron oxidation of phenolics, aromatic amines, and other electron-rich substrates with the concomitant reduction of O_2 to H_2O. We have recently characterized an unusual laccase from *Sclerotinia sclerotiorum.* Here, we report on the expression of this laccase as a response of environmental stress. Various carbon sources as well as nitrogen sources for *Sclerotinia sclerotiorum* were tested, by monitoring the laccase activity, mycelium weight and morphology.

The pH of the medium appeared to be very important both for growth and for laccase production; importantly, the pH of the culture medium prior to sterilization had a notable effect, even if at inoculation the pH was adjusted back to other values – suggesting that the composition of the medium is affected by sterilization in a manner that generates stressors or inducers for the culture. *Sclerotinia sclerotiorum* tolerates well alkaline pH up to pH 9, by a mechanism where it decreases it to a final value of almost 3.5 (physiological pH), with different kinetics depending on the initial pH value; the fungus does not develop at all bellow pH 3. Laccase production is maximum between pH 5-7.

Extracts of *Chelidonium majus* as well as of yeast were found to be laccase inducers in *Sclerotinia sclerotiorum* through stress pathways as proved by mycelium morphology and protein profile. Fractionation experiments suggest that the nature of the inducer from yeast is an organic molecule, while in the *Chelidonium majus* extract it is probably a mixture of alkaloids or polyphenols as suggested by other authors which describe its antifungal properties. Overall, the extracellular laccase produced by this organism appears to be regulated by several variables such as nutrients, pH and other inducers.

Acknowledgement: *Financial support from POSDRU/88/1.5/S/60185 – "Innovative doctoral studies in a knowledge based society" is gratefully acknowledged by ACM.*

Keywords: *Sclerotinia sclerotiorum; laccase induction; protein regulation; Chelidonium majus; yeast extract;*

P-0053

PANURGINES, NOVEL ANTIMICROBIAL PEPTIDES FROM THE VENOM OF WILD BEE PANURGUS CALCARATUS AND THEIR INTERACTIONS WITH PHOSPHOLIPIDS VESICLES

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Three novel antimicrobial peptides, named panurgines (PNG), were isolated from the venom of wild bee *Panurgus calcaratus*. One of them is dodecapeptide LNWGAILKHIIK-NH_2 (PNG-1). The next two are almost identical peptides containing 25 amino acid residues and two intramolecular disulfide bridges LDVKKIICVACKI**X**PNPACKKICPK-OH (X = K, R PNG-K or PNG-R). All peptides exhibited antimicrobial activity against Gram-positive and Gram-negative bacteria, antifungal activity and low haemolytic activity. We prepared 11 analogues of PNG-1 with the aim to improve its biological properties and a linear analogue of PNG-R to elucidate importance of disulfide bridges for its activity.

In the second part of the study, we followed the effect of panurgines on the degree of membrane disruption by observing the leakage of fluorescence dye (calcein) entrapped in artificial phospholipids vesicles. Specifically, we investigated membrane interactions of PNGs with negatively charged vesicles 1:2 DOPC/DPPG and 1:2 DOPC/DOPG as a general model of bacteria membrane and 15:80:5 DOPC/DOPG/CL as a possible model for a membrane of *Bacillus subtilis*. The membrane interaction of PNGs was also investigated on uncharged DOPC vesicles as potential model membrane for erythrocytes. PNGs exhibited weak dye-leakage activity for neutral vesicles, while they effectively induced dye leakage in the presence of negatively charged vesicles. These results indicate that PNGs have stronger potency to disrupt bacteria-mimicking anionic membranes than those which mimic eukaryotic cell membrane.

Keywords: *antimicrobial peptides; phospholipids vesicles;*

P-0054

BIOINDUCED INVESTIGATION ON METAL ION – HYDROXAMATE SYSTEMS

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Hydroxamic acids are among the most well studied compounds due to their significance in so many fields. For example, due to their good metal binding capability, they are effective inhibitors of many metalloenzymes, including MMP-s or ureases. The inhibitory effect is in direct correlation with the coordination of the hydroxamate function to the metal ion situating in the active centre of the metalloenzyme. This is one reason, why transition metal ion-hydroxamate complexes have been in the focus of interest and interaction of metal ions with various hydroxamic acids and also the factors determining the interaction have been investigated in Debrecen for many years. Because there have been only a few data on Mn(II)- and Co(II)-hydroxamate complexes in the literature, our recent work has focused on such types of systems. Numerous mono-, di- and two trihydroxamate based natural siderophores. desferrioaxamine B (DFB), and desferricoprogen (DFC), have been involved into the study, in which the stoichiometry, the thermodynamic and redox stabilities of the complexes have been determined. Relaxometric measurements on the Mn(II)-systems provided also interesting information about the intramolecular motions in the Mn(II)-siderophore complexes.

Surprisingly, oxidation of Mn(II)- and Co(II)-siderophore complexes at high pH resulted the formation of extremely high stability complexes. The stability of the Mn(III) complexes are close, while that of the Co(III) complexes is higher than the stability of the corresponding Fe(III) species. Whether does it mean the possibility of disruption of the microbial iron-uptake in the presence of these metal ions? This question and all the results obtained for the Mn(II) and Co(II) complexes are planed to discuss in a presentation.

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Keywords: *hydroxamate complexes; equilibrium study; hydroxamate based siderophores; manganese and cobalt ions; thermodynamic and redox stability;*

P-0055

DNA DAMAGE RECOGNITION BY XPA/RAD14 IN NUCLEOTIDE EXCISION REPAIR

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DNA is constantly subjected to damaging agents such as UV- or γ-irradiation, as well as oxidation and hydrolysis or chemical carcinogenes. To avoid degeneration of the genetic information, nature developed a variety of DNA repair pathways to repair the resulting lesions. One of the main genome maintenance systems in eukaryotes is the Nucleotide Excision Repair (NER). NER is a multistep process that includes damage recognition, assembly of repair factors at the damaged site, dual incision on either side of the lesion containing oligonucleotide, which results in an excision of the lesion, followed by DNA synthesis to fill the gap. A defective NER response in humans leads to a high predisposition to skin cancer (*Xermoderma Pigmentosum*).[1] XPC/Rad 4 is known to detect disrupted duplex structures[2], whereas XPA/Rad14 is thought to be required for the binding of bulky DNA adducts generated by chemical carcinogens, like aromatic amines. We want to elucidate the exact mechanism of the recognition of bulky adducts by NER recognition factors. Therefore we investigate the binding affinity of the human XPA and its yeast homolog Rad14 to DNA containing bulky lesions by EMSA. The crystal structure of Rad14 in complex with an acetylaminofluorene-dG containing oligonucleotide will give us insight into the mechanism of damage recognition of bulky adducts in NER.

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Keywords: *NER; XPA/Rad14;*

P-0056

MONITORING CHANNEL PROTEIN–MEDIATED TRANSLOCATION OF ARGININE–RICH PEPTIDES BY A SUPRAMOLECULAR SENSING ENSEMBLE

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The influx of xenobiotics such as antibiotics, peptides, and other biologically relevant molecules through channel proteins, or in general, through lipid bilayers, is crucial for medicinal, biotechnological, and analytical applications and also for understanding the translocation processes.[1–4] Consequently, assays to detect the flux of molecules through these channels with high sensitivity, versatility, and scalability for high-throughput screening is in high demand in the pharmaceutical industry, and biochemical research laboratories.[5–7] However, the techniques for accurate monitoring of this process are limited, in particular those allowing continuous real-time measurement of concentration changes.

Drawing inspiration from supramolecular tandem assays,[8–11] we introduce herein a simple yet effective fluorescence based strategy to study the diffusion of molecules through the membrane or channel proteins, namely supramolecular tandem membrane assay. The underlying principle is to encapsulate a macrocyclic host and a fluorescent probe inside the liposomes. This leads to a compartmentalization of the sensing ensemble inside the proteoliposomes, such that one can follow the permeation of analytes in real-time via fluorescence, because the host/dye complex will respond only to analytes which enter into the inside of the vesicles, where they displace the dye from the macrocycle and trigger the fluorescence response.

Owing to their impermeablity through the lipid membrane, a anionic macrocyclic receptor *p*-sulfonatocalix[4]arene (CX4) and a highly fluorescent dye lucigenin (LCG) were selected as a host/dye reporter pair to investigate the translocation of protamine, an arginine-rich antimicrobial peptide through a bacterial outer membrane channel protein F (OmpF).[10, 12, 13] The translocation of protamine into the liposomes was monitored as a time-resolved increase in fluorescence intensity due to the release of the dye LCG from the CX4 cavity. Furthermore, using the tandem membrane assay method, we were able to screen for other translocating analytes, the activity of mutagenized OmpF, and the effect of channel modulators on the translocation process.

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Keywords: *peptides; liposomes; membrane proteins; fluorescence; fluorescent dyes; supramolecular chemistry; macrocycles; lipids;*

P-0057

USE OF A NON-HEME IRON PEROXIDASE IN HEMOGLOBIN AND HEMERYTHRIN-BASED BLOOD SUBSTITUTES

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Hemoglobin-based potential artificial oxygen carriers have been described and examined extensively.However, their applicability so far has been limited due to known *in vivo* toxicity issues. As many of these issues can be linked to oxidative stress, strategies were proposed for limiting this toxicity by adding antioxidant small molecules or enzymes to chemically-derivatized or encapsulated hemoglobin. Hemerythrin has distinctly smaller reactivity than hemoglobin towards oxidative and nitrosative stress agents, and also shows a remarkably smaller tendency to generate toxic free radicals in such reactions.

The non-heme iron peroxidase, rubrerythrin (Rbr), shows as an interesting feature the ability to reduce hydrogen peroxide without involving strongly-oxidizing and free-radical-creating powerful oxidants such as Compounds I and II (formally Fe(IV) in contrast with heme-containing peroxidases and catalases. Morevoer, the K_m for hydrogen peroxide is two orders of magnitude lower in Rbr compared to peroxidases and catalases. Therefore, it may be used as a useful ingredient in protein-based artificial oxygen carriers. Hemoglobin (Hb) and hemerythrin (Hr), can each be co-polymerized with rubrerythrin using gluteraldehyde as cross-linking agent. These co-polymers show additional peroxidase activity compared to Hb-only and Hr-only polymers, respectively. Reported here are protocols for chemical crosslinking of hemerythrin and hemoglobin with small amounts of rubrerythrin, leading to products with increased capability for removing hydrogen peroxide, offering promise as less toxic artificial oxygen carriers/blood substitutes.

Tests on human umbilical vein endothelial cells (HUVEC) reveal slightly better performance of the Rbr co-polymers compared to controls, as measured at 24 hours but not at later times.

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Keywords: *blood substitutes; Rubrerythrin; co-polymers; hemoglobin; hemerythrin;*

P-0058

CONFORMATIONAL STABILITY OF A NOVEL AMYLOID-BETA TETRAMER TOPOLOGY

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The amyloid-β (Aβ) peptide is a key molecule in the pathogenesis of Alzheimer's disease (AD), the most common neurodegenerative disorder. Originally, the Aβ fibrils were postulated to be the neurotoxic agents for a long time, because an increased presence of extracellular amyloid plaques, composed primarily of insoluble Aβ fibrils, is found in the brain of affected patients. Recent studies, however, showed a higher cytotoxicity for small Aβ oligomers than for the Aβ fibrils so that these soluble Aβ oligomers are moving to the centre of interest now.

Because of the unstable and noncrystalline nature of these species, obtaining structural information for small oligomers is an experimentally challenging task. Novel structural insight was obtained from a recent crystal structure of a tetramer formed by the amyloidogenic residues 18-41 of the Aβ peptide. To enhance stability, this fragment was genetically engineered into the CDR3 loop region of a shark Ig single variable domain antibody.

Since the respective crystal structure is stabilized by the antibody moiety, we investigated, whether the respective topology also represents a stable fold for the isolated Aβ-peptide.

We performed molecular dynamics simulations (200ns) in explicit solvent for the isolated tetrameric amyloid-β fragment in two different lengths (17-40 or 17-42) and the derived dimer and monomer structures.

In contrast to the tetramer of $A\beta_{17\text{-}40}$, we observed a stable dynamical behaviour of $A\beta_{17\text{-}42}$: The extension of the antiparallel β-sheet (through the residues 41 and 42) is responsible for the enhanced structural stability in $A\beta_{17\text{-}42}$.

In summary, our results suggest that the novel tetrameric structure represents a stable oligomer conformation for the longer and more neurotoxic $A\beta_{42}$ species and thus could be a new target in rational drug design aiming at the prevention of toxic oligomer formation.

Keywords: *Amyloid beta-peptides; Molecular dynamics; Protein structures; Aggregation; Medicinal chemistry;*

P-0059

THE IMPACT OF THE BISPIDINE STRUCTURE ON THE STABILITY OF THEIR CU(II) COMPLEXES

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Rigid bispidine (3,7-diazabicyclo[3.3.1]nonane) derivatives have been shown to form stable complexes, particularly with first row transition metal ions.[1] The variable number, type and position of donor groups provide a variety of tailor-made coordination sites for specific metal ions. Furthermore, the bispidine skeleton opens suitable pathways to introduce biomolecules, which are important in view of the pharmaceutical targeting of such complexes. Due to these interesting features, bispidines are predestined as attractive bifunctional chelating agents for the development of target-specific copper-based radiopharmaceuticals. In this perspective, a hexadentate bispidine ligand consisting of pyridine units in the positions C-2, C-4, N-3, and N-7 was conjugated to the tumour-seeking peptide bombesin. The ^{64}Cu-labeled bioconjugate is accumulated in human prostate tumors to allow clear visualization of the tumor tissue.[2]

In order to optimize the radiopharmaceutical behavior, further bispidine ligands have been developed with different denticity (tetra-, penta, hexadentate) with pyridine and/or methoxypyridine donor groups and with the possibility to introduce functionalities, such as targeting units and fluorescence labels in view of pharmaceutical targeting as well as dual labeling (PET and optical imaging).

These ligands and the important properties of their Cu^{II} complexes, e. g. stabilities, exchange kinetics and partition coefficients (^{64}Cu: octanol/water) will be reported.

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Keywords: *ligand design; imaging agents; copper;*

P-0060

ELECTROCHEMICAL AND SPECTROSCOPIC STUDIES OF THE INTERACTION BETWEEN THE NEUROLEPTIC DRUG,GABAPENTIN, AND DNA

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The interaction between gabapentin (GP), a neuroleptic drug, and DNA was investigated. Cyclic voltammetry and different spectroscopic methods (UV/Vis spectrophotometry, spectroflourimetry and Circular dichroism) were used to study the process. The oxidation current of GP was considerably decreased in the presence of calf-thymus DNA. The negative shift of the peak potential in cyclic voltammetry suggested an electrostatic mode of binding. The binding constant (K-=-8.33 × 10^3 mol^{-1} L) was obtained from voltammetric data with a standard Gibbs free energy change, ?G°, of -21.99 kJ mol^{-1} at 25 °C which indicated the spontaneity of the binding interaction. A hyperchromic effect in the maximum absorption band of DNA as well as quenching in fluorescence experiments were observed in the presence of GP. The values of binding constants obtained from UV absorption, spectrofluorimetry and voltammetric measurements, were in close agreement.

Keywords: *gabapentin; DNA; Cyclic voltammetry; Spectroscopy; Binding constant;*

P-0061

POTENT BENZENESULFONAMIDES AGAINST THE PREDOMINANT COMMUNITY-ASSOCIATED METHICILLIN-RESISTANT STAPHYLOCOCCUS AUREUS STRAIN USA300

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Since first isolated in 1880, a Gram positive bacteria *Staphylococcus aureus* (*S. aureus*) has remained the leading source of bacterial infections in human and in animal worldwide. The treatment of *S. aureus* infection becomes more complicated due to the emergence of antibiotic resistance. The community-associated methicillin-resistant *Staphylococcus aureus* (CA-MRSA), which acquires resistance to the commonly used beta-lactam antibiotics such as penicillin, poses a serious threat in terms of infection control. The pathogen can colonize in healthy individuals and easily transmit via skin-to-skin contacts. The epidemic MRSA PFGE strain type USA300, in particular, has become the predominant CA-MRSA strain causing serious skin and soft tissue infections as well as life-threatening diseases. The USA300 isolates have been currently recognized and responsible for infections in many continents, including Europe. As several USA300 isolates showed reduced susceptibility to vancomycin in addition to occasional resistance to the combination therapy, trimethoprim-sulfamethoxazole. The dramatic spread of MRSA USA300 in addition to the emergence of the currently used antibiotics resistance has greatly heightened the need for discoveries of novel therapeutics. Here in, we investigated the structural features required for the growth inhibition of *S. aureus* and MRSA USA300 strain SF8300. The small focused chemical library was designed and synthesized in a few steps from commercially starting materials. The pathogen susceptibility results led to the discovery of the potent *S. aureus* and MRSA USA300 growth inhibition *N*-(3,5-bis(trifluoromethyl)phenyl)-4-bromobenzene sulfonamide [MIC = 5.6 mg/L] and other effective sulfonamides. Structure-activity correlations revealed that the benzene sulfonamide bearing electron-withdrawing substituents were essential for inhibiting pathogen growth effectively. Interestingly, these potent sulfonamides were also able to completely inhibit growth of the sulfonamide-resistant MRSA strain (COL), implicating that these active sulfonamides may inhibit bacterial growth via alternative mechanisms differed from the folate pathway inhibition, known for typical sulfonamide antibiotics.

Keywords: *Methicillin-resistant Staphylococcus aureus (MRSA); USA 300 CA-MRSA; Benzenesulfonamides;*

P-0062

REGULATORY MECHANISM OF PHOSDUCIN FUNCTION

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Phosducin (Pdc), a regulatory and highly conserved 30 kDa acidic phosphoprotein, is present in a variety of cell types, with especially high expression in retinal photoreceptors and pinealocytes. Pdc regulates the G-protein signaling by competing with Ga for binding to G$\beta\gamma$ subunits. The ability of Pdc to bind to G$\beta\gamma$ depends on its phosphorylation state as only unphosphorylated Pdc binds G$\beta\gamma$ tightly. Phosphorylation of Pdc within the N-terminal part inhibits its binding to G$\beta\gamma$ through unclear mechanism involving the interaction between Pdc and the regulatory 14-3-3 protein. The 14-3-3 proteins are conserved regulatory proteins expressed in all eukaryotic cells from yeast to human.

In this work, we studied interactions between phosphorylated Pdc and 14-3-3 using analytical ultracentrifugation, dynamic light scattering and time-resolved fluorescence spectroscopy. Our results show that: (**i**) Pdc and 14-3-3 form a stable complex with 1:2 molar stoichiometry; (**ii**) the molecule of Pdc is unfolded; and (**iii**) the 14-3-3 protein binding significantly affects the structure of both the N- and C-terminal domains of Pdc.

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Keywords: *Protein-protein interactions; Biophysics; Fluorescence spectroscopy; Protein structures;*

P-0063

TEMPLATE-DIRECTED SYNTHESIS IN 3'- AND 5'-DIRECTION WITH REVERSIBLE TERMINATION

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Chemical primer extension (CPE) involves the elongation of a synthetic primer on a DNA or RNA template using active esters of nucleoside-5'-monophosphates.[1] This reaction is known for RNA primers,[2] DNA primers with a 3'-terminal 3'-amino-2',3'-dideoxynucleoside,[3-5] and DNA primers with a 3'-terminal 2'-amino-2',3'-dideoxynucleoside.[6] The latter version of CPE has been performed with fluorophore-labeled monomers, allowing for the optical read-out of sequences without enzymes.[7,8] Also, catalyzed CPE occuring within minutes or seconds have been reported.[9] Here we report a method that we refer as template-directed synthesis with reversible termination. This method uses azidomethyloxycarbonyl (Azoc) moieties as protecting group which can be removed under non-denaturing conditions,[10] as well as a magnetic solid support that allows for the noncovalent binding of the template and the primer oligonucleotide. Tenfold, controlled and stepwise synthesis of oligonucleotides in template-directed fashion is demonstrated both in 3'- and 5'-direction.[11]

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Keywords: *DNA; solid-phase synthesis; protecting groups;*

P-0064

DEVELOPMENT OF NEW NO-ASA-DERIVATIVES FOR THE TREATMENT OF CHRONIC LYMPHOCYTIC LEUKEMIA (CLL)

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NO-ASA was originally developed by *NicOx* to treat human colon cancer.[1] It was found later that this Aspirin-derivative is effective for treating many other human cancers, such as prostate, pancreatic, lung, skin, breast, and bladder cancers, and is also suitable for the treatment of type-2-diabetes and the cardioprotection of animal hearts.[3] *Kreuzer et al.* reported that NO-ASA is also very effective against chronic lymphocytic leukemia (CLL).[3] According to the current mechanistic scenario NO-ASA is initially metabolized to different active compounds. The key compounds are quinone methide (QM) and nitrate anion. QM contributes the major part to the anticancer effect of NO-ASA, due to the fact that it is a very reactive Michael acceptor. Various studies point out that quinone methide reacts with many nucleophiles, alkylates the DNA and proteins (like glutathion). The nitrate anion effects S-nitrosylation and tyrosine nitration. All reactions lead to modifications in the cell-signaling pathways and ultimately result in the apoptosis of cells.[2,4] Based on the promising results achieved with NO-ASA, we decided to syn-the-s-ise several new NO-ASA-de-rivatives. Our efforts resulted in the discovery of some more potent NO-ASA-derivatives. Several *in vitro* assays and *in vivo* xenograft nude mice models showed sig-nificantly improved and sele-ctive cytotoxicity of some of our com-pounds in comparison to NO-ASA. For future, mechanistic studies, we are intending to label our compounds in particular with regard to bio-orthogonal reactions and mass spectroscopy.

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Keywords: *Cancer; Synthesis design; Bioorganic chemistry; Biotransformations; Cytotoxicity;*

P-0065

STRUCTURAL ASSEMBLY OF HEXOSAMINIDASE COMPLEX

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Background: Fungal β-*N*-acetylhexosaminidases EC 3.2.1.52) are inducible extracellular glycosidases involved in many biological processes. The native enzyme from *Aspergillus oryzae* CCF 1066 is composed of two propeptides (each 10 kDa) and two catalytic units (each 65 kDa). The propeptides are noncovalently associated with the catalytic units and are essential for the enzyme activity.

Objectives: In this study we would like to uncover the position where the propeptide is associated with the catalytic unit.

Methods: β-*N*-acetylhexosaminidase was purified from the medium of the producing organism. For EDC (1-Ethyl-3-(3--dimethylaminopropyl) carbodiimide) experiment the enzyme was transferred by gel filtration to 50mM Pyridine pH 5.5, 150mM NaCl and for DSG (disuccinimidyl glutarate) experiment to 50mM Triethylamine carbonate pH 7.5. After the cross-linking reaction was over, the products of enzyme were separated by SDS electrophoresis. In gel digestion was performed and the resulting peptides were analyzed by LC-ESI FT MS (Agilent 1200, APEX-Ultra)

Results: To obtain good reproducibility and high yields of cross-linking reactions, different types and concentrations of cross-linking reagents together with optimization of enzyme concentrations in the reaction was performed. The best results were achieved by using DSG and EDC reagents. Enzyme concentration was set to 0.5 mg/ml. The ratio of cross-linking agents over the enzyme was 100 fold access of EDC and 50 fold access of DSG. By LC-ESI FT MS analysis were found several intermolecular (A80-S96 with I347-E365) and few intramolecular cross-links (A102-K114 with D409-Y434). Obtained results are in a good agreement with X-ray diffraction data.

Conclusions: Combinating chemical cross-linking and high resolution mass spectrometry we uncover the region of propeptide-catalytic unit ineraction. Moreover we revealed that the structural changes of the catalytic unit depend on the presence/absence of the propeptide molecule.

Acknowledgement: *This work was supported by grants P207/10/1040 and P207/10/1934 of the Czech Science Foundation.*

Keywords: *Glycoproteins; Enzyme models; Mass spectrometry; X-Ray diffraction;*

P-0066

SPECTRAL ANALYSIS OF SECONDARY METABOLITES PRODUCED IN FUNGAL INTERACTIONS

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Fungal competition for territory and resources is inevitable in habitats with overlap between the niches of different species or strains. Interactions between wood-decaying basidiomycetes are excellent examples of such competition and the outcome determines the size of territory held by one mycelium, and hence access to nutrients. It is a major impetus of community change, and affects decay rates in woodland ecosystems. Competition is brought about by antagonistic mycelial interactions which elicit mycelial morphology, metabolic, secondary metabolite release and extracellular enzyme pattern changes.

The basidiomycete studied, *Schizophyllum commune*, is a white-rot fungus which is most widely distributed world-wide. The abundance of *S. commune* can not only be attributed to its incredible mating ability (more than 23,000 different sexes), but also to its superior competition ability. It has been noted that *S. commune* produces secondary metabolites, especially in the interaction zone or zone of contact with competitor species. The nature of these compounds is unknown and may be the result of the action of the fungal oxidative enzymes in response to stress caused in the face of a stimulans excreted from the competitor.

We attempted to elucidate the composition of the compounds produced during these interactions using Raman micro-spectroscopy. The principle is that Raman spectra contain information on molecular vibrations providing a highly specific fingerprint of the molecular structure and biochemical composition of cells and tissues. Spectra are obtained non-invasively without interference from water. The employment of external labels is not necessary and the sample requires little or no preparation. Moreover, the coupling of Raman spectroscopy with microscopy (Raman Micro-spectroscopy) enables high spatial resolution (below ~ 1 μm) and sensitivity. Using particularly resonance Raman spectroscopy, we show the presence of Indigo in the zones of interaction of the fungi.

Keywords: *Raman spectroscopy; Structure elucidation; Dyes/Pigments;*

P-0067

STRUCTURE CHANGE OF JUVENILE HORMONE BINDING PROTEIN FROM SILKWORM HEMOLYMPH

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Juvenile hormones (JHs) are acyclic sequiterpenoids which contain an unsaturated methyl ester and a terpenoid backbone with an epoxide distal to the ester. JH regulates many processes, including the growth, development, metamorphosis and reproduction of insects. The JH actions are initiated by transport of JH in the hemolymph as a complex with JH-binding protein (JHBP) to target tissues. The concentration of JHBP in the hemolymph varies in relation to development but almost always exceeds the concentration of JH by some orders of magnitude. It has been estimated that more than 99% of the JH molecules in hemolymph are bound by JHBP. Here, we report structural properties of JHBP based on the solution and crystal structures of apo and JH-bound JHBP. CD measurements in buffer solution suggested that apo-JHBP exists in equilibrium of multiple conformations. The crystal structures of the apo and JH-bound JHBP have an unusual fold with hydrophobic pockets. JH-binding form results in the fully closed structure where the bound JH is completely buried inside the protein. JH-bound JHBP opens the gate helix to release the bound hormone likely by sensing the less polar environment at the membrane surface. Our results reveal the structural basis for JH transport by JHBP in hemolymph, the first essential process of the JH signal transfer mechanisms.

Keywords: *Juvenile hormone binding protein; CD spectroscopy; X-ray crystallography;*

P-0068

DEVELOPMENT OF FIRST INHIBITORS FOR BETAINE-HOMOCYSTEINE S-METHYLTRANSFERASE 2

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Only three human enzymes are able to methylate homocysteine to yield methionine: methionine synthase, betaine-homocysteine S-methyltransferase (BHMT) and betaine-homocysteine S-methyltransferase-2 (BHMT-2). BHMT-2 is a zinc metalloenzyme that catalyzes the transfer of a methyl group from S-methylmethionine (SMM) to l-homocysteine yielding two molecules of l-methionine. SMM is not synthesized in mammalian organism but is a universal component of their diet. The human BHMT-2 has 73% amino acid identity to BHMT. Similarly to BHMT, BHMT-2 is highly expressed in liver and kidney. BHMT-2 proved to be a very unstable enzyme. Physiological functions of BHMT-2 remain unknown also because no selective BHMT-2 inhibitor is available.

The aim of this study was to purify and stabilize human recombinant BHMT-2 and to design, synthesize and discover first potent and selective inhibitors of the enzyme. The enzymes were expressed in transfected *E. coli* cells and purified using chitin affinity chromatography. The inhibitors were designed to mimic the hypothetical transition state of BHMT-2 substrates, SMM and homocysteine. All the inhibitors were prepared from l-methionine. In general, cleavage of the l-methionine methyl group by sodium in liquid ammonia generated a solution of l-homocysteine, which was alkylated *in situ* by appropriate halogenide.

In our study, we purified human recombinant BHMT-2 stabilized by co-purification with human recombinant BHMT. Then we synthesized first BHMT-2 inhibitors, which were tested with BHMT-2 and BHMT. Among these compounds, we identified a highly potent inhibitor, (2S,8RS,11S)-5-thia-2,11--diamino-8-methyldodecanedioic acid, which represents the first selective inhibitor of BHMT-2. Moreover, this inhibitor inhibits BHMT only weakly. We determined its IC_{50} and K_i^{app} towards BHMT-2 and IC_{50}towards BHMT.

BHMT-2 was highly stabilized by co-purification with BHMT, which raises questions about co-oligomerization of the enzymes *in vivo*. Potent and selective BHMT-2 inhibitors will be useful in future *in vivo* studies of physiological functions of the enzyme in animal models.

Keywords: *enzyme catalysis; inhibitors; alkylation;*

P-0069

NOVEL IN VITRO NONCELL BASED MODEL FOR PREDICTING PHOSPHOLIPIDOSIS

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Phospholipidosis (PLD) is a lipid storage disorder characterized by the accumulation of phospholipids within cells and has been found to be induced by several drugs. Several studies have indicated that cationic amphiphilic drugs (CADs) are responsible for inducing this lipid accumulation in cells. In drug discovery and development, the accumulation of drugs in critical tissues such as brain, eye, liver, and heart are of major concerns and it is clearly a disadvantage when compared to a competitor without PLD indication.

Several *in silico*[1, 2], *in vitro* cell based[3] and noncell based [4, 5] methods to evaluate PLD-inducing potential with low and middle throughput have been available until recently. In the present study we have evaluated a well-known permeability model, a PAMPA (Parallel artificial membrane permeability assay) for predicting of PLD potency.

Typical artifacts of *in vitro* models are caused by metabolism of investigated drugs which modifies PLD potency by at least two ways. In the present study we have investigated these metabolic effects of selected compounds and their metabolites by our new pH-gradient PAMPA system.

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Keywords: *drug discovery; Phospholipids;*

P-0070

SIMULTANEOUSLY DETERMINATION OF MEROPENEM AND CLAVULANIC ACID BY USING DERIVATIVE SPECTROSCOPY

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Meropenem as a carbapenem analog belongs to the group of β-lactam antibiotics, while clavulanic acid is a β-lactamses inhibitor, which increases the antibacterial activity of β-lactam antibiotics. Recent studies reported that the connection of meropenem and clanulanic acid showed the unique antibacterial activity, including effectiveness in the treatment of *Mycobacterium tuberculosis* [1].

The aim of the studies was to develop derivative spectroscopy for the simultaneously determination of meropenem and clavulanic acid. The application of derivative spectroscopy solved the problem of overlapping of absorption spectra of meropenem and clavulanic acid. In derivative spectroscopy, meropenem was determinated at $\lambda_{mer} = 324$ nm and clavulanic acid at $\lambda_{clav} = 285$ nm. The method was validated in terms of selectivity (the evaluation of changes of meropenem and clavulanic acid concentration for degraded samples), precision, accuracy, linearity. Limits of determination (LOD) and quantitation (LOQ) were established.

The experimental results demonstrate that meropenem and clavulanic acid can be determined in their binary mixture and in the presence of their degradation products, by the first-derivative spectroscopy using the zero-crossing technique. The method meets all validation parameters and is in accordance with current trends of ‘green pharmaceutical analysis’.

Acknowledgements: *This study was supported by a grant from the Foundation for Polish Science (no. VENTURES/2011-8/7).*

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Keywords: *Antibiotics; UV/Vis spectroscopy; Green chemistry;*

P-0071

EFFECT OF NANOPARTICLES ON HUMAN EPIDERMAL KERATINOCYTES AND HUMAN DERMAL FIBROBLASTS

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Background: Wound healing processes create a very complex system of connected reactions which influence each other. Normal healing takes place in four basic stages: homeostasis, inflammation, reparation and remodelling. A lot of types of cells (neutrophils, monocytes, lymphocytes, fibroblasts and keratinocytes etc.) and mediators (cytokines and matrix metalloproteinases) are involved into the healing. The current investigations are shown that silver ions and nanoparticles have antibacterial and anti-inflammatory properties as well as gold nanoparticles.

Objectives: In this work, we have been studied the influence of nanoparticles (colloidal silver and gold solutions) on biomarkers involved in the wound healing process on human epidermal keratinocytes and human dermal fibroblasts.

Methods: Both types of cells were isolated from samples of skin with the informed consent of the Ethical committee of the University Hospital in Olomouc and the patient’s consent. Cytotoxicity of nanoparticles (0.013–50 ppm; 24–72 h) was evaluated by cell viability (MTT) assay. The effect of nanoparticles on selected biomarkers interleukin-6, tumour necrosis factor alpha, cyclooxygenase-2, matrix metalloproteinase-1, matrix metalloproteinase-3 and matrix metalloproteinase-13 was determinated by ELISA techniques and western blot analysis.

Results and conclusion: Our results showed that the colloidal silver decreased cell viability in dose-dependent manner (1–50 ppm; 24–72 h) while colloidal gold did not show cytotoxic effect on both cell types. The effect of nanoparticles on selected inflammatory markers in human epidermal keratinocytes and human dermal fibroblasts will be discussed.

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P-0072

ANTICANCER ACTIVITY OF PHTHALAZINYL HYDRAZONES

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Heteroaryl hydrazones are compounds with significant biological activity including anticancer activity. Therefore we designed set of phthalazinyl hydrazones for testing their activity against cancer cells. Anticancer activity evaluation on the human promyelocytic leukemia cells (HL60) and mouse mammary carcinoma cells (4T1) showed that some phthalazinyl hydrazones have significant inhibitory effect against both cancer cell lines. Complexation studies toward biologically important metal ions (Cu^{2+}, Co^{2+}, Cr^{3+}, Fe^{2+}, Fe^{3+}, Mn^{2+}, Ni^{2+}, Zn^{2+}) at biologically relevant conditions show general ability to bind Cu^{2+}, Co^{2+}, Ni^{2+} and Fe^{3+} (with some exceptions) and rarely Zn^{2+} and Fe^{2+}. There is not any clear correlation of binding ability with anticancer activity; however many derivatives able to bind Zn^{2+} display very high activity ($IC_{50} < 1$ µM for HL60) and opposite way all derivatives without binding ability towards Co^{2+} do not display any significant activity ($IC_{50} > 10$ µM for both lines). Phthalazinyl hydrazones are known to display tautomerism; QD/MD calculations in aqueous media show significant preference of hydralazine form in contrast to preference of phthalazone form described in literature (obtained from *in vacuo* calculations). Calculations also show that metallo-complexes of derivatives are relatively planar and thus potentially allow intercalation into DNA in contrast to derivatives themselves. This is in good agreement with experimental observation that metallo-complexes of many derivatives display ability to interact with DNA but derivatives themselves do not.

Acknowledgement: *Financial support was provided from Specific university research (MSMT No. 21/2012, Grants A1_FCHI_2012_003 and A2_FCHI_2012_021 provided by IGS VSCHT) and the Grant Agency of the Czech Republic (Grants No. GA203/09/1311 and GAP303/11/1291).*

Keywords: *Hydrazones; Schiff bases; Antitumor agents;*

P-0073

SOLUBLE SYNTHETIC MINIAMYLOIDS

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Based on the proposed contact surfaces between individual β-amyloid peptides (Aβ) within fibrillar aggregates[1] we synthesized soluble Miniamyloids as chemically consistent dimers, trimers and other oligomers, respectively. Selected Aβ fragments were linked in different relative orientations by a combination of protecting group strategy and click chemistry. Several unnatural amino acids were synthesized and incorporated into the Miniamyloids to assemble the antiparallel and parallel oligomers of the peptide strands.

Aβ derivatives are characterized by their notoriously high aggregation tendency. To prevent fiber formation and to improve solubility, anionic and cationic amino acids were incorporated aside the native sequence. By varying the charge pattern and in combination with the different arrangements of the peptides strands a broad set of Miniamyloids was obtained. These peptides are a valuable and unique tool to understand how naturally occurring antibodies against Aβ (nAbs-Aβ)[2] recognize oligomeric Aβ and Aβ aggregation itself.[3] For instance they can be used for affinity chromatography experiments to specify the pool of polyclonal nAbs-Aβ.

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Keywords: *amyloid-ß peptide; protein aggregation; Alzheimer's disease;*

P-0074

SUPRAMOLECULAR LIGANDS OF PROTEINS

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Proteins bind ligands commonly by docking them to sites evolutionary designed for binding. However some strongly assembled organic compounds have been recently found to form complexes penetrating as clusters of molecules into protein body outside the binding site. The large ligands which assume the shape of ribbon-like or rode-like supramolecular form affect significantly structure and function of proteins. Congo red is an example. The several or more assembled molecules of this dye adhere firmly to polypeptide backbone penetrating in between protein chains of β-conformation. The penetration and complexation is basically limited to low stability protein regions and is usually connected with the replacement of some polypeptide fragment from its native locus to make room for the ligand. Partly unfolded proteins are typical objects of binding supramolecular ligands but some native proteins of structure altered due to function-derived constraints may also become susceptible for binding. Bivalent antibodies bound to large antigens belong to such proteins. The constraints arise due to the imposed fitting of both antibody arms to randomly distributed antigenic determinants. V domains of antibodies are those which bind Congo red. The increased freedom of movements within domain results from replacing N-terminal polypeptide from β-plate by noncovalently stabilized ligand. It facilitates fitting of CDR loops to antigenic determinants increasing significantly the affinity of antibody to antigen.

The selective binding of Congo red to immune complexes with the preserved micellar nature of the dye allows the carriage of many compounds and drugs incorporated by intercalation. It raised the idea of using supramolecular systems as carriers in immunotargeting technique. The confirmation of its applicability *in vitro* and *in vivo* is shown on the poster.

Keywords: *supramolecular ligand; Congo red; immunoglobulin;*

P-0075

NOVEL SCREENING ASSAY FOR A,B-UNSATURATED CARBONYL COMPOUNDS TOWARDS THEIR HEME OXYGENASE-1 INDUCTION

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Heme oxygenase 1 (HO-1) is a redox sensitive, inducible stress protein converting heme to CO, iron and biliverdin, which is further reduced to bilirubin by biliverdin reductase. As a member of the cytoprotective phase II enzymes the transcription of HO-1 is regulated by the Keap 1/Nrf2/ARE signaling pathway. α,β-Unsaturated carbonyl compounds possess Michael acceptor activity and can react with nucleophilic sulfhydryl groups of the Nrf2-complexing chaperon Keap1. Thereby the Nrf2 regulated antioxidant-responsive element (ARE) is activated which leads to a transcriptional induction of HO-1. Various natural products and synthetic molecules containing the α,β-unsaturated carbonyl moiety reveal an induction of the anti-inflammatory, antioxidant and cytoprotective enzyme HO-1.

A novel HO-1 activity assay was established in order to discover new potent HO-1 inducing agents. The cell-based assay is a highly sensitive high-throughput screening method that determines HO-1 activity based on the quantification of bilirubin in whole cell lysates via ELISA. A diverse group of natural products was tested and could be assessed concerning its HO-1 induction behaviour.

Keywords: *biological activity; immunoassays; high-troughput screening; antioxidant; inflammation;*

P-0076

EXPLOITATION OF VEGFR2 TK SALT BRIDGE CONTAINING POLAR POCKET FOR DEVELOPMENT OF ARYLAMINOOXAZOLE INHIBITORS WITH IMPROVED ACTIVITIES

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An interaction analysis, molecular modelling and docking have been used to design new derivatives of VEGFR2 inhibitor **AAZ** (N-[5-(ethylsulfonyl)-2-methoxyphenyl]-5-(3-pyridin-2--ylphenyl)-1,3-oxazol-2-amine, PDB: 1Y6A). A small Salt Bridge Containing Polar Pocket (SBCPP) consisting from Lys866, Glu883 and Phe1045 amino acid residues was found to be situated over an internal aromatic ring of **AAZ** ligand. SBCPP pocket is currently present in DFG-out VEGFR2 tyrosine kinase complexes hosting Type I ligand (PDB: 1Y6A, 1Y6B, 3C7Q). Intermolecular interactions between SBCPP pocket and **AAZ** derivatives were considered to ensure a good VEGFR2 affinity for new compounds. Proposed substances **BM1-BM3** were synthesised and their enzymatic and cellular VEGFR2 inhibition activity determined together with **AAZ**, **sorafenib tosylate** and **sunitinib L-malate**. Calculated binding energies for **AAZ**, **BM1-BM3** and experimental IC_{50} values were found in a good agreement. Of the analogues investigated, **BM1** and **BM2** demonstrated significant enzymatic nM inhibitory activity against the VEGFR2 kinase comparable to that of **sorafenib tosylate** and **sunitinib L-malate**, respectively.

Acknowledgements: *we are grateful for the gift of drug active compounds: sorafenib tosylate (Nexavar®, Bayer HealthCare Pharmaceuticals) and sunitinib L-malate (Sutent®, Pfizer Inc.) to both Bayer HealthCare and Pfizer companies, respectively. For molecular docking and structure predictions, we thank to Biomagi, Slovakia. The COST action CM0602 (AngioKem) and CM1106 (StemChem) for research networking is also acknowledged. This work was supported by VEGA grant 2/0112/10. Dissemination of international collaboration was supported by Joint Interface Third-Cycle Degrees in Chemistry (PhDChem) 502271-LLP-1-2009-1-GR-ERASMUS-ECDSP.*

Keywords: *Angiogenesis; Drug design; Salt Bridge Containing Polar Pocket; arylaminooxazoles; VEGFR2 tyrosine kinase;*

P-0077

SELECTIVE INHIBITION OF JMJD2 HISTONE DEMETHYLASES BY ZINC-EJECTION

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The oxygenase JMJD2A, recently identified as a possible anti-cancer target, catalyzes the demethylation of N^{ε}-lysyl methylation on histone tails. Most JMJD2A inhibitors developed to date chelate the active site Fe(II) and also compete with 2-oxoglutarate, a common cofactor for all dioxygenases, making selective inhibition of JMJD2A difficult to achieve.

Structures of JMJD2A revealed a Cys_3-His Zn(II) binding site close to the N^{ε}-methyl lysine-residue binding site, which is not present in other dioxygenases. We reasoned that the catalytic activity of the JMJD2 histone demethylases might be inhibited by compounds known to act as Zn(II) ejectors from proteins.

Our objective was to demonstrate that Zn(II) ejection by selected sulphur and selenium-containing compounds is a viable approach for selective inhibition of JMJD2 histone demethylases. MALDI-MS based peptide turnover assays were thus employed for measuring a decrease of catalytic activity upon treatment with Zn(II) ejectors, differential scanning fluorimetry (DSF)-based protein stabilization assay was used to measure the extent of structural destabilization by Zn(II) ejectors, and Zn(II)-selective fluorophore Fluozin™-based Zn(II) ejection assay was used to demonstrate the loss of Zn(II) from the protein structure upon treatment with Zn(II) ejectors.

Using this methodology, we have successfully demonstrated Zn(II) ejection as a novel approach to achieving selective inhibition of the JMJD2 histone demethylases over other dioxygenases. In particular, commercially available drug disulfiram, used in treatment of alcoholism, was found to be a potent inhibitor of JMJD2A acting by Zn(II) ejection mechanism. In conclusion, this new approach to selective oxygenase inhibition may prove useful in probing the complexity of epigenetic modifications and the regulatory enzymes that catalyze them.

Keywords: *Inhibitors; Enzyme catalysis; Structural biology; Drug discovery;*

P-0078

QUANTITATIVE ANALYSIS FOR THE DNA STABILITY TOWARD THE DEVELOPMENT OF NEW FUNCTIONAL MATERIALS

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DNAs have been attracting attention as the advanced materials such as biosensors, biodevices, and biocircuits due to specific base-pairing interactions of DNAs. However, for DNA materials to become practically applicable, finding a medium in which they are stable for long time periods at room temperature is an important bottleneck in this field. Room-temperature ionic liquids (ILs) have generated tremendous interest as non-volatile media that provide favourable environments for a wide range of chemical and biochemical reactions. Choline dihydrogenphosphate (choline dhp) with 20% dissolved water is hydrated IL, which has been demonstrated to be a good solvent for proteins and DNAs for ensuring long-term stability. It is considered that the hydrared IL should be useful as a medium developing DNA materials because the hydrated IL can keep the activity of biomolecules for long time. However, its detail effect on the DNAs remains unclear.

Here, we have investigated quantitatively thermodynamic stabilities of DNA duplexes, triplexes and G-quadruplexes by ultraviolet melting in the solution containing choline dhp. Choline dhp induced a drastic change in the DNA stabilities depending on their structures compared with an aqueous solution. In the presentation, we will discuss the stability changes of DNA structures from the perspective of thermodynamic parameters for the DNA structure formations. Moreover, we will show our recent works regarding quantitative analyses for the transcription, translation and telomerase elongation reactions toward the development of new functional materials.

Keywords: *DNA; Thermodynamics; Ionic liquids;*

P-0079

SYNTHESIS, ANALYSIS AND ANTIOXIDANTPROPERTIES OF SCHIFF BASE INDOLE-AMINO ACID DERIVATIVES

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Increased levels of reactive oxygen species attributed to oxidative stress have been found to be responsible for the development of some vital diseases such as cardiovascular, neurodegenerative and autoimmune diseases. Recently, it was observed that melatonin is a highly important antioxidant, and melatonin analogues are under investigation to find out improved antioxidant activity. In this study, 14 indole amino acid and N-protected amino acid derivatives were synthesized and elucidated spectrometrically. To investigate the antioxidant activity of the synthesized compounds and to compare with melatonin, butylhydroxytoluene and vitamin E, lipid peroxidation inhibition and 2,2-diphenyl-1-picrylhydrazyl radical-scavenging activities were tested. The results indicated that the synthesized new indole amino acid derivatives have similar activities to melatonin in 2,2-diphenyl-1-picrylhydrazyl radical-scavenging activity assay but more potent activities in lipid peroxidation inhibition assay.

Keywords: *indole; amino acid; synthesis; analysis; antioxidant;*

P-0080

MAGIC ANGLE SPINNING (MAS) NMR IN LIFE SCIENCES

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Magic angle spinning (MAS) averages out chemical shift anisotropy and weak dipolar couplings and allows the acquisition of high-resolution NMR spectra of solids. MAS solid state NMR (ssNMR) is nowadays widely used for the investigation of the structural and dynamical properties of integral membrane proteins, as well as a for the characterization of immobilized large soluble proteins, thus overcoming the size limitations imposed by the large line widths associated to slow molecular tumbling in solution.[1] Immobilization of soluble proteins is generally obtained via microcrystallization or PEG precipitation of the protein. MAS ssNMR of proteins has been essentially restricted to ^{13}C-detection and, less commonly, ^{15}N-detection experiments. MAS NMR can also be used to obtain solid state NMR spectra on sedimented samples. Relatively large proteins in solution, spun in NMR rotors for solid samples at typical ultracentrifugation speeds, sediment at the rotor wall, providing samples with limited reorientational capability. The resulting spectra are comparable in quality with those of the best microcrystalline samples.[2,3]

Technical improvements that permit very fast MAS have started allowing the acquisition of ^{1}H-detected spectra of microcrystalline and sedimented samples. On the other hands, slow MAS represents a useful approach for high-resolution ^{1}H NMR metabolic profiling of intact tissues.

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P-0081

PHARMACOPHORE MODELING AND 3D-QSAR STUDIES OF ACRIDONES AS CHEMOSENSITIZING AGENTS IN CANCER

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In the present study we have identified an efficient pharmacophore from a set of 38 acridones which reverts HL-60/DX cell line. Identified pharmacophoric features such as one hydrogen bond acceptor, one hydrophobic region, a positive ion group and three aromatic rings i.e, AHPRRR. Ligand based 3D-QSAR was performed by employing partial least square regression analysis which gave a regression coefficient R^2 of 0.98 and Q^2 of 0.86, and Pearson-R of 0.95. Another pharmacophore model of same compounds with same set of pharmacophoric features with different 3D spatial arrangement showed that 0.95 (R^2), 0.87 (Q^2) and 0.94 (Pearson-R). Molecular docking study was performed for fluoro acridones against calmodulin dependent *c*AMP phosphodiesterase (PDE1c) in order to identify the possible protein ligand interactions and results thus obtained were compared with *in-vitro* data, good correlations were found between *in-silico* and *in-vitro* results.

Keywords: *Acridone; 3D-QSAR; Pharmacophore; Docking; MM/GBSA;*

P-0082

ANTIOXIDANT PROFILE OF RED CLOVER (TRIFOLIUM PRATENSE L.)

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It is well-known that polyphenolic compounds are responsible for the potential antioxidant activity and radical scavengig capacity of plant. In this context, there is an increasing interest in the benefical health effects of plant derived phytoestrogens with special focus on isoflavones. Recent research has shown that Red clover (*Trifolium pratense* L.) extract contain significant high amounts of all four major estrogenic isoflavones genistein, daidzein and their methyl ether derivatives biochanin. A and formononetin which are known for their potential bio-active antioxidant properties and radical scavenging capacity. This research reports the antioxidative activities of four different extracts and determination of dominant compound in extract which showed the best scavenging capacity for the free radical species such as: 2,2-diphenyl-1-picrylhidrazyl ($DPPH^{\cdot}$), nitric-oxide ($NO^{\cdot}$) and super oxide anion ($O_2^{\cdot-}$). Free radical scavenging capacity was determined on the basis of the calculated values of $IC_{50.}$ The greatest antioxidant effect has an extract which shows the lowest value of IC_{50}. In our case it is ethyl acetate extract: DPPH (IC_{50}=17.82µg/mL), $NO^{\cdot}$ (IC_{50}=20.35µg/mL) and $O_2^{\cdot-}$ (IC_{50}=12.90µg/mL). For this reason, this extract was used for the determination of dominant components by HPLC analysis. Predominant bioactive compounds in extract are isoflavones: daidzein, genistein, formononetin, biochanin A, such as their glycosides and they are corresponding with literature data. Considering the mentioned above results, isoflavones are probably responsible for the antioxidant activity of Red clover. Ethyl acetate extract is suitable for isoflavones extraction, because they are less polar than some other flavonoides which are responsible for antioxidant activity.

Keywords: *Antioxidants;*

P-0083

DETECTION OF THE ANTIOXIDATIVE ACTIVITY IN COMPOUNDS LACKING THE TYPICAL STRUCTURAL DETERMINANTS

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At the present day task-oriented search of new antioxidants (AOs) is somewhat one-sided. Hydrogen donors (e.g., phenolic or thiol groups), reducing and chelating fragments are supposed as usual determinants of direct antioxidative activity (AOA). Therefore, new AOs were sought mostly among phenols, thiols and chelators. However, El Bakkali et al. have recently shown AOA can be found in aromatics without the said structural determinants. Aim of this study was to evaluate AOA for various compounds lacking typical pharmacophores. To this purpose we synthesized 20 derivates of adenine or quinazoline with substituents containing the aromatic rings and hydrogen bond acceptors. None of these compounds contained phenolic, thiol or carboxylic groups. None of them showed reducing activity with phosphomolybdic acid. Prediction of AOA by PASS (http://www.pharmaexpert.ru/passonline/) was negative for all synthesized compounds. However, 5 of 20 tested compounds exhibited AOA detected by the ABTS cation radical decolourization test. Range of averadge EC_{25} values was 3,74-8,18 µM for five active compounds. Thus AOA of the new compounds was slightly less than AOA of the well-known AOs gallic and ascorbic acids (values of EC_{25} were 1,32 and 2,23 µM respectively). Three of newly found AOs (VMA-10-09, VMA-10-10 and VMA-10-20) contains the same substructure which absent in inactive compounds. This substructure is expressed as CC(=O)NC1=CC=C(C=C1)N(C)C in the SMILES notation or [#6]-[#6](=[#8])-[#7]-c1ccc(cc1)-[#7](-[#6])-[#6] in the SMARTS notation. Biologically relevant AOA of VMA-10-09 and VMA-10-10 was tested by copper-induced oxidative haemolysis assay. Both VMA-10-09 and VMA-10-10 prevented RBC lysis better than quercetin or 2,6-di-tert-butyl-4--methylphenol (BHT) taken at the same concentration. Hence we identified a new structural subfragment might be the determinant of AOA.

Keywords: *Antioxidants; Biological activity; Drug discovery;*

P-0084

COBALT-BINDING CAPACITY OF THE BOVINE SERUM ALBUMIN TREATED IN VITRO BY VARIOUS OXIDIZING AGENTS

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Various properties of the serum albumin are often used as basis of a number of clinical laboratory tests. One of them is the ACB test proposed by Bar-Or et al. to detect myocardial ischemia. Hypothesis which underlies this test is reduction of the serum albumin cobalt-binding capacity (CoBC) due to oxidative modification during the blood passes through hypoxic myocardium. However, genuine 'ishemia-modified albumin' (IMA) has not been purified yet. Moreover, controversal data about clinical significance of the ACB test has risen. We proposed diagnostic ambiguity of the ACB test might be concerned with IMA propeties which have not determinated clearly. We examined whether various oxidizing agents could change CoBC of the serum albumin diversely. The bovine serum albumin (BSA) was used as model protein. We measured CoBC by colourimetric dithiothreitol assay. The tested oxidizing agents were the Fenton's reagents and NaOCl. All tested oxidizing agents caused weak accumulation of dinitrophenylhydrazine-reactive carbonyls and depletion of the thiol groups in BSA. However, effects of oxidizing agents on CoBC were different. The copper-based Fenton's reagent (H_2O_2 + $CuSO_4$) significantly reduced CoBC of treated BSA in comparison with native BSA. Effect of the iron-based Fenton's reagent (H_2O_2 + Mohr's salt) on CoBC was negligible. On the contrary, treatment of BSA by NaOCl increased CoBC value. Although the effect of NaOCl seems surprising, the chemical modification of ε-NH_2-groups of Lys by acetylation, deamination, succinylation, or reaction with 2,4-dinitrobenzenesulphonic acid is known to raise the cobalt binding by human serum albumin. Similarly NaOCl modifies ε-NH_2-group of Lys forming the chloramine groups. We suppose the NaOCl-induced increase of BSA CoBC can be produced by elimination of positive charges of lysines in the protein molecule. Hence, we showed oxidants can act as both inhibitors and stimulants of cobalt-binding activity of serum albumin.

Keywords: *Proteins; Oxidation; Redox chemistry;*

P-0085

SYNTHESIS AND STRUCTURE-ACTIVITY RELATIONSHIPS OF BIS-3-CHLOROPIPERIDINES AS BIFUNCTIONAL DNA ALKYLATING AGENTS

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Bifunctional alkylating agents such as chlorambucil and melphalan represent an important class of clinical cancer chemotherapeutics. The antitumor antibiotics azinomycin A and B have the ability to alkylate and cross-link DNA. However, their poor chemical stability suggests that these natural products are unlikely to progress as therapeutic candidates. Yet they can act as lead structures from which to develop potentially useful new molecules.[1]

Due to our interest in developing more effective bifunctional alkylating agents, we designed novel bis-3-chloropiperidines based upon the azinomycins backbone.[2] The nitrogen mustard moiety is more stable and the alkylating functions generated via intermediate aziridinium ions are positioned in a similar distance as has been observed for the azinomycins.[3, 4] To examine the relationship between structural modifications and DNA alkylating rates it appeared appealing to introduce aromatic units that might facilitate DNA interactions. Accordingly, we synthesised a series of derivatives and evaluated the alkylating properties by performing a DNA cleavage assay. Furthermore, *in vitro* cell cytotoxicity studies of these compounds were carried out using the MTT method. The biochemical and cytotoxicity results as well as the synthetic approach to bis-3-chloropiperidines will be presented.

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Keywords: *Antitumor agents; DNA cleavage; Structure-activity relationships;*

P-1018

RATIONALLY DESIGNED NIR-FLUORESCENT NANOPARTICLES FOR BIOANALYTICAL APPLICATIONS

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Current trends in the life sciences are fluorescence-based techniques and concepts for signal amplification and multiplexing strategies to increase the overall detection sensitivity and to enable the ratiometric and simultaneous detection of several analytes.[1]

This can be successfully achieved with fluorophore loaded or labeled particles preferably emitting in the visible or near-infrared (NIR) spectral region. The detection within the diagnostic window (650 to 950 nm) is advantageous to reduce scattering effects and absorption from tissue and blood components and signal contributions from autofluorescence.[2, 3] Moreover, fluorophore incorporation into particles can reduce unspecific interactions between the dye molecules and the surrounding medium and can also minimize their potentially cytotoxic effects. Furthermore, encapsulated NIR dyes often show an improved photochemical and thermal stability as well as enhanced fluorescence quantum yields in polar and protic solvents like water.[4] For hydrophobic dyes with very low solubility in aqueous media, encapsulation presents the only strategy for their use in biologically relevant environments.

Here, we present the synthesis and characterization of bright NIR-fluorescent polystyrene nanoparticles by a simple one-step staining procedure which can be applied to all bioanalytically relevant dye classes including xanthenes, cyanines, squaraines, oxazines, and BODIPYs.[5] The resulting particles with various surface functions and spectral properties have great potential for cellular imaging and biomarker targeting. Applications as ratiometric nanosensors for several analytes like oxygen,[6] and as labels for lifetime multiplexing detection schemes will be exemplary shown.

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P-0086

FORMATION OF GREEN RUST SULFATE AND CARBONATE IN THE PRESENCE OF ZN USING TIME-RESOLVED IN SITU SMALL– AND WIDE–ANGLE X-RAY SCATTERING

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Green rusts (GR) nanoparticles are highly reactive iron minerals that typically form under weakly acidic to alkaline conditions in suboxic environments. GR have been shown to significantly reduce the solubility and mobility of many toxic and radioactive species in the environment, including Cr, U, Se, Ni and Zn. GR is a lamellar double hydroxide solid with Fe^{2+} and Fe^{3+} cations in the main hydroxide layer and anionic species (e.g., SO_4^{2-}, CO_3^{2-}) occupying the interlayer domain.

The formation mechanisms of green rust sulfate (GR-SO_4) and carbonate (GR-CO_3) were determined using an *in situ* approach combining time-resolved synchrotron-based Wide– and Small–Angle X-ray Scattering with highly controlled chemical synthesis and electrochemical monitoring of the reaction. Both GR materials were coprecipitated under anaerobic conditions. The reaction in both systems proceeded *via* a three stage reaction. During the first stage schwertmannite [$Fe_8O_8(OH)_{4.5}(SO_4)_{1.75}$] precipitated directly from solution at pH 2.8 - 4.5. With increasing pH (> 5) Fe^{2+} ions adsorb to the surface of schwertmannite and catalyse its transformation into goethite during the second stage of the reaction. In the third stage, the hydrolysis of the adsorbed Fe^{2+} ions on goethite initiates its transformation to GR-SO_4 at pH near 7. A fourth stage was identified at pH > 8.6 in the GR–CO_3 system which involves an interlayer SO_4^{2-}/CO_3^{2-} ion–exchange process leading to the formation of the GR–CO_3 phase. Evidences on the incorporation of Zn^{2+} into the molecular structure of GR are also presented.

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Keywords: *Wide Angle Scattering; Green Rust; schwertmannite; Synchrotron; Coprecipitation;*

P-0087

PHOTOLYSIS OF SULFAMETHOXYPYRIDAZINE IN VARIOUS AQUEOUS MEDIA: AEROBIC BIODEGRADATION AND PHOTOPRODUCTS IDENTIFICATION BY LC-UV-MS/MS

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In recent years, interest is growing continuously in the occurrence, fate, and possible effects of pharmaceutical compounds residues in the environment. Sulfonamides are one of the most frequently used antibiotics in human and veterinary medicines worldwide especially in Asia and Africa. Therefore mitigation processes are of interest. Photodegradation and biodegradation are the potentially significant removal mechanisms for pharmaceuticals in aquatic environments.

The photolysis of sulfamethoxypyridazine (SMZ) using a medium pressure Hg-lamp was evaluated in three different media: Millipore water pH 6.1 (MW), effluent from sewage treatment plant pH 7.6 (STP), and buffered demineralized water pH 7.4 (BDW). Identification of transformation products (TPs) was performed by LC-UV-MS/MS. The biodegradation of SMZ using two tests from the OECD series was studied: Closed Bottle test (CBT; OECD 301 D), and Manometric Respirometry test (MRT; OECD 301 F).

The results showed that SMZ was removed completely within 128 min of irradiation in the three media, but they differ only in the degradation rate. However, no dissolved organic carbon (DOC) removal was observed in BDW and little DOC removal was observed in MW and STP, thus indicating the formation of nearly abundant TPs. Analysis by LC-UV-MS/MS resulted in the detection of up to six TPs of photolysis in MW, but only one of them was detected in STP and BDW. The observed difference may be due to pH or buffer salts differences. The hydroxylation of SMZ represents the main photodegradation pathway. In biodegradation tests, it was found that SMZ was not readily biodegradable in both CBT and MRT so it may pose a risk to the environment.

Advanced oxidation process for SMZ and biodegradation tests for photodegradation samples will be performed. Further research on SMZ and its TPs, including environmental samples analysis, as well as toxicity tests are strongly recommended to know its environmental impact.

Keywords: *Sulfonamides; Photolysis; Biodegradation; Transformation products; Aquatic environment;*

P-0088

REMOVAL OF POLLUTING METAL CATIONS FROM WATER USING A SIO$_2$ MATRIX ENTRAPPED LIGAND – N,N' DI(2-HYDROXY-4,6 DI-TERBUTYL-BENZYL) IMIDAZOLIDINE

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Toxic metal ions removal from water by using chelating polymers is of great importance due to their high selectivity, efficiency and easy handling. The aim of this study is to prepare a novel, N,N' di(2-hydroxy-4,6 di-terbutyl-benzyl)imidazolidine (L) bonded solid columns that can absorb various heavy metal cations. The solid chelating beads are prepared by incorporating the ligand to SiO$_2$ matrix via the sol-gel biphasic method. The introduction of organic functional groups to the silica matrix produces a new organofunctional-bonded-silica gel surface. The adsorption of Cu^{2+}, Ni^{2+} and Cd^{2+} to the chelating inorganic support was examined and was found to be very efficient. The results suggest an integrated process which links metal cations involving anionic groups inherent in the sol gel matrix (ionic atom exchange mechanism) as well as ligation by the “fixed” ligand, L, (coordination mechanism).

Keywords: *sol gel;*

P-0089

POLYMETAL(FE,AL)N-ZEOLITE TUFF(CLN) COMPOSITES AS COAGULANTS FOR WASTEWATER TREATMENT

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Coagulation/flocculation is preferred in the primary purification processes of water and in industrial wastewater treatment mainly due to the operation ease, high efficiency and cost effectiveness. Also, it uses less energy than alternative treatments. The most commonly used coagulants are aluminium or iron(III)-based salts[1, 2].

The work aims to obtain composites with coagulation properties by valorising the red mud waste from the aluminium industry and the roumanian zeolite tuff (66-75% clinoptilolite) and to verify their efficiency in treating hydrocarbon-polluted waters.

The polymetal $(Fe,Al)_n$ -zeolite tuff(CLN) composites were obtained by treating the red mud (RM) waste

with acid solutions (HCl, H_2SO_4) of different concentrations, at pH values of 3-5.5, followed by the modification of the zeolite tuffs with polymetallic prehydrolyzed salts obtained at 45–80 °C with $(Fe, Al)_n$/CLN ratios of 1/0.5 -1/10. The solid phase of the modified zeolite tuff was separated from the mix by filtration and drying.

The processing conditions of the red mud(acid concentration, pH, RM/HCl, H_2,SO_4) for obtaining polymetallic prehydrolyzed salts and those for the $(Fe, Al)_n$- CLN composites influence both the structural characteristics determined by DRX, XRF FTIR, Raman spectroscopy, SEM and the wastewaters treatment process efficiency.

The new $(Fe, Al)_n$-CLN composites efficiency in the hydrocarbon-polluted waters(C_{12}-C_{20}, TOC=100-500 mg/L) treatment process was studied by Jar tests, at 25, 45 °C. The experimental results emphasise the coagulant properties of the composites. Using the composites(0.3-0.4 mM metal content), generates an increase in yield for the reduction of turbidity, TOC, UV254nm and settling times by 50%, 67-87%, 80% and 45% respectively, all compared to the situation in which only the conventional "Alum" coagulant was used.

The simplification of the overall treatment process and the cost-effectiveness are considered as the major advantages of the composite coagulants.

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Keywords: *coagulation/flocculation; wasterwater; red mud;*

P-0090

OZONATION PRODUCTS OF TRICLOSAN FORMED IN ADVANCED WASTE WATER TREATMENT

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Triclosan is an antimicrobial agent which has recently gained increasing interest because of its potential impacts on environment and public health. The high removal rate in biological wastewater treatment plants (> 90%) may not be enough as this compound is very effective on non target aquatic organisms. However the emitted amounts of Triclosan are present in surface waters with concentrations of 1-10 ng/L. Thus it is studied on whether ozonation of waste water may give improved results.

In this study the reaction of Triclosan by aqueous ozone is investigated. Removal efficiency of Triclosan by ozone and kinetic data for the different steps are presented. Transformation products such as chlorophenols and hydroxy-triclosan derivatives are identified by GC-MS and HPLC-MS. Probably Triclosan is oxidized in two ways: addition of hydroxyl-groups and breaking of the ether bridge between the two aromatic rings. Structural elucidation was performed by advanced tandem mass spectrometry. The toxicity of selected transformation products in cellular systems was studied as a basis of an assessment. In total the concentrations go down drastically, however some of the transformation products are of concern.

Keywords: *triclosan; ozone; oxidation; waste water treatment;*

P-0091

DIOXINS IN HUMAN MILK FROM DIFFERENT REGIONS OF FRANCE: PILOT OF THE FRENCH LONGITUDINAL STUDY OF CHILDREN (ELFE)

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Surveillance of the exposure to chemicals among pregnant women and their child is particularly important and constitute one of the objectives of the on-going Elfe (French longitudinal study of children) cohort study, by the use of biomarkers.

The present work focused on the determination of polychlorodibenzodioxines (PCDD), polychlorodibenzofuranes (PCDF) and dioxin-like polychlorinated biphenyls (DL-PCBs) levels in the breast-milk of the mothers included in a pilot study of Elfe, carried out in the fall of 2007 in a random sample of children of several counties in France.

A set of 35 compounds were tested: seven 2,3,7,8-substituted PCDDs, ten 2,3,7,8-substituted PCDFs, 12 DL-PCBs (four non-*ortho*-PCBs, eight mono-*ortho*-PCBs) and six NDL-PCBs.

Fourty four samples of breast-milk were liquid-liquid extracted and analyzed with gas chromatography coupled to high resolution mass spectrometry (GC-HRMS). The limits of detection and quantification were optimized to obtain a good selectivity and sensitivity.

Mothers were aged from 24 to 41 years old (mean and median: 32 years) and 50% (n=22) were primiparous or secundiparous. The geometric mean concentration for total TEQ (PCDD/Fs and DL-PCBs), was 24.25 pg TEQ/g lipids if expressed in WHO1998-TEQ and 17.74 in WHO2005-TEQ.

The comparison of these results with those from a previous national study conducted in 1998 shows that proportion of PCDDs was 78% of PCDD/Fs in 2005 versus 50% in 1998. For the sum of the 6 NDL-PCBs, the geometric mean concentration in milk was 176.3 ng/g lipids. The mean fat concentration in breast milk was 25.1 g/L (range from 6 to 46.7 g/L). When the comparison concerns only the primaparous mothers in 1998 and 2007, the decrease of the mean of PCDD/F levels was equal to 40%.

Keywords: *health; dioxin; environment;*

P-0092

PREPARATION AND CHARACTERIZATION OF TI/PT/PBO$_2$-TIO$_2$ ANODES FOR IBUPROFEN DEGRADATION

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Metal oxides are a promising class of anode materials that have been investigated in the last decades. Among the studied oxides, PbO_2 already proved to be very efficient in the degradation of organic pollutants, eliminating them from solution by mechanisms of conversion/combustion[1]. It can even compete with BDD anodes, giving similar removal rates for organic pollutants degradation, with the advantage of having much lower preparation cost. However, it presents lower service-life than BDD anodes. Thus, to increase anodes life time, prior to PbO_2 depositions titanium substrates were platinized and, to allow photoelectrocatalysis applications, during the electrodeposition of PbO_2, TiO_2 nanoparticles were also incorporated in the film. Ti/Pt/β-PbO_2-TiO_2 electrodes were prepared by thermal electrochemical method[2, 3]. The electrodes were structural and morphological characterised by XRD and SEM that confirm the presence of β-PbO_2+TiO_2 phases. The prepared Ti/Pt/β-PbO_2-TiO_2 anodes were used in the electrodegradation of 100 ppm ibuprofen aqueous solutions, with Na_2SO_4 5 g L^{-1} as electrolyte. The electrodegradation assays were run with 200 mL of solution and different currents densities, j, were tested, 10, 20 and 30 mA cm^{-2}, during 6 h. The samples collected during the electrochemical assays were analysed for the following parameters: Chemical oxygen demand (COD), total organic carbon (TOC) and UV-Visible absorption spectrophotometry. After 6 h assay, the best removals of Abs_{224nm}, COD and TOC were obtained at the highest current density tested and were, respectively, 95, 76 and 63%.

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Keywords: *Ibuprofen; anodic oxidation; PbO2;*

P-0093

EFFECTS OF UV-B RADIATION AND VITAMIN C ON THE ANTIOXIDANT DEFENSE SYSTEMS IN WINTER WHEAT (TRITICUM AESTIVUM CV.DOGU-88) AND BARLEY (HORDEUM VULGARE TOKAK 157) SEEDLINGS

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The stratospheric ozone decrease has heightened concern over the ecological implication of increasing solar UV-B (280–315 nm) radiation on agricultural production and natural plant ecosystems. UV-B effects on plants include physiological damage to the photosynthetic apparatus, damage to DNA, effects on membranes and morphological damage as evidenced by stunting of plants, leaf discoloration and decreased vegetative biomass and grain yield. Therefore, antioxidant is likely to reduce the oxidative burden, hence tissue damage. Vitamin C is one of the most widely available and affordable nonenzymatic antioxidant molecules that have been used to mitigate oxidative damage. It is an important water-soluble antioxidant in biological fluids in wheat and barley. It readily scavenges physiological ROS such as superoxide, hydroxyl, and aqueous peroxyl radicals, as well as nonradical species such as singlet oxygen and ozone, as well as reactive nitrogen species (RNS).

In this study, the effects of UV and their combinations of UV and vitamin C on the activities of antioxidant enzymes were researched in the leaves of wheat (*Triticum aestivum L.* Dogu 88) and barley (*Hordeum vulgare* Tokak 157) cultivars. Fifteenday-old wheat and barley seedlings were treated with UV radiation (240 nm, 3 day) prior to vitamin C treatment (20 °C). Supplementary UV-B radiation and UV-B+Vitamin C significantly decreased chlorophyll contents but total phenol contents was increased in both wheat and barley leaves. The activities of enzyme extracts; polyphenol oxidase, catalase, paraoxonase and peroxidase were determined in the wheat and barley leaves both under normal, UV-B (<315 nm) and UV-B + vitamin C conditions at 3 days. The antioxidant enzymes weren't affected and showed an enhanced activities in peroxidase, paraoxonase and polyphenoloxidase except catalase in UV-B and then vitamin C irradiated wheat and barley seedlings. UV-B and then vitamin C-treated the winter wheat and barley seedlings try to counteract high level of reactive oxygen species produce under UV-B stress through the increased activities of antioxidant enzyme. It is suggested that vitamin C try to counteract high concentrations of oxygen species produced under UV-B radiation stress through increase in UV absorbing compound and antioxidant enzymes.

Keywords: *Oxidative damage; environmental stress; vitamin C; peroxidase; catalase; polyphenol oxidase; paraoxonase; phenolic compaunds;*

P-0094

WATER-SOLUBLE MAIN IONS IN PRECIPITATION OVER THE SERBIA

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Wet deposition refers to the natural processes by which material is scavenged by atmospheric hydrometeors and is consequently delivered to the Earth's surfaces. The challenge of understanding processes ranging from the microscale to the macroscale makes wet deposition one of the most complex atmospheric processes[1].

Most parts of Serbia have a temperate continental climate. During the colder part of the year, precipitation is generally associated with the penetration of low pressure systems from the west (extra-tropical cyclones coming from the Atlantic Ocean). During the summer most of the precipitation is convective type, conditioned by the emergence of local instability and thunderstorm systems.

Precipitation samples collected from 2001 to 2010 at seven sampling stations(Serbia) were analyzed on water-soluble ions. Ion concentrations were determined by ion chromatography.

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Keywords: *precipitation; water-soluble ions; Serbia;*

P-0095

SILICA FUME MODIFICATION FOR ITS USE AS ALTERNATIVE ADSORBENT MATERIAL FOR CADMIUM FROM AQUEOUS SOLUTIONS

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The presence of heavy metals in the environment is one of the major concerns because of their toxicity and threat to human life. Therefore, the effective removal of heavy metals from industrial wastewater is among the most important issues for many industrialized countries. Removing of cadmium from aqueous solutions has been studied using silica fume waste material after its modification with bacteria called *Methylobacterium radiotolerans*. Batch adsorption experiments have been performed as a function of pH, contact time and adsorbent dose. The experimental investigation results show that bacteria modified-silica fume has a high level of adsorption capacity for removing cadmium ions. The results revealed that cadmium is considerably adsorbed on the bacteria modified-silica fume. Consequently, it is concluded that the bacteria modified-silica fume can be successfully used for the removal of the cadmium ions from the aqueous solutions with heavy metals.

Keywords: *Wastewater; Silica fume; Bacteria-modified silica fume; Cadmium removal; Adsorption studies;*

P-0096

BACTERIA-MODIFIED RED MUD FOR ADSORPTION OF CADMIUM IONS FROM AQUEOUS SOLUTIONS

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Cadmium is widely used in industry and it enters the environment from electroplating, smelting, alloy manufacturing, pigments, plastic, cadmium-nickel batteries, fertilizers, pesticides, mining, pigments and dyes, textile operations and refining industries. Cadmium is recognized as a highly toxic element and a serious environmental contaminant; therefore, its removal from water is very important. Removal, separation and enrichment of heavy metal ions in aqueous solutions play an important role for the environmental remediation of wastewater.

The present study describes removal of cadmium from aqueous solutions using bacteria-modified red mud waste material as low cost adsorbent. Batch adsorption experiments have been performed as a function of pH, contact time, temperature and adsorbent dosage. The optimum results were obtained at pH 4.0, contact time of 60 min, temperature of 30 ºC and an adsorbent dose of 1 mg/mL. Experimental equilibrium and kinetics data were fitted by Langmuir and Freundlich isotherms and pseudo-first-order and pseudo-second-order kinetics models, respectively. The results show that the equilibrium data follow Langmuir isotherm and the kinetic data follow pseudo-second-order model. The maximum adsorption capacity obtained from Langmuir isotherm is 83.034 mg/g. The results show that the bacteria-modified red mud can be used for the treatment of aqueous solutions containing cadmium as an alternative low cost adsorbent.

Keywords: *Wastewater; Red mud; Bacteria-modified red mud; Cadmium removal; Adsorption studies;*

P-0097

TREATMENT OF OLIVE OIL MILL WASTEWATER BY SILICA-ALGINATE-FUNGI BIOCOMPOSITES

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Olive oil mill wastewater (OMW) is a liquid waste which constitutes a major environmental problem due to the presence of a wide variety of pollutants[1]. In order to mitigate the environmental impact of these effluents, efficient treatment systems have been developed to reduce the COD, color, organic compounds, and toxicity[2, 3]. In this study, we firstly report the potential of a treatment strategy for OMW (from Portugal and Morocco) by biocomposites of silica-alginate-fungi (Pleurotus sajor caju and Trametes versicolor). The treatment by biocomposites was processed on three steps for the efficient removal of the compounds, i.e., through the adsorption of reactants on the monolithic structure and diffusion to the biological active sites, biodegradation by the fungi, and diffusion of the products resulting from the biodegradation. We found potential capacity to remove organic compounds, color, COD and toxicity; the T. versicolor biocomposites were the most effective and responsible for the reduction in color, COD, and total phenolic content after 29 days of treatment. On the other hand, the toxicity reduction on Portuguese OMW was minimal, but the use of biocomposites on the Moroccan OMW caused a 9.5- to 19-fold reduction in toxicity. Furthermore the proposed treatment strategy shows great potential for tertiary treatment of OMW.

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Keywords: *environmental chemistry; toxicology;*

P-0098

IMPACT OF NATURAL ORGANIC MATTER ON THE TOXICITY OF NANOPARTICLES

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As of now, the risk posed by nanoparticles (NP) for the environment has not been well examined. The effects that can occur if NP encounter microorganisms (MO) in the environment are of special interest as bacteria play a critical role in ecosystems. In environmental aquatic systems the interaction of NP with water constituents such as calcium, sodium and natural organic matter (NOM) is of high relevance. NOM is omnipresent in aqueous systems and can significantly change the properties of pristine NP concerning their stability and their toxicological impact[1, 2].

In this contribution, we follow the hypothesis that the adsorption of NOM on the surface of NP renders their physical-chemical behavior and will have an effect on their toxicity towards MO.

In batch systems the adsorption of fulvic acid (FA) on SiO_2-CL NP and the associated change in their zeta potential was investigated. The FA served as a model for NOM and was isolated from a brown water lake (Lake Hohloh/Black Forest, Germany) using a standard method given in[3]. The toxicity of the NP was determined against *Pseudomonas putida* (gram-negative) and *Lactobacillus plantarum* (gram-positive).

The adsorption of FA onto the NP could be fitted using the Langmuir approach. The SiO_2-CL NP have a point of zero charge at $pH = 9$. Therefore, the adsorption was significantly higher at pH-values below 9 with a maximum FA loading of 160 ± 23 µg/mg. The zeta potential of the NP changes from +30 mV to -20 mV (at $pH = 7$) caused by the adsorption of the FA.

Most MO have a negative zeta potential at neutral pH-values. Due to the electrostatic attraction between the pristine NP and MO, the NP cover the surface of the MO and impair their proliferation [4]. Based on the adsorption of the FA and the change in the zeta potential, the toxicity of the SiO_2-CL was diminished in the presence of FA.

This detoxification effect is of general importance for aquatic systems.

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P-0099

AIR POLLUTION STUDIES IN RUSSIA BASED ON MOSS ANALYSIS: PAST, PRESENT AND FUTURE

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The use of mosses as biomonitors of atmospheric deposition of trace metals and radionuclides in Russia started more than 30 years ago in connection with the development and problems of the nuclear and military-industrial complexes in Siberia and the Urals. In the 1990s, within the framework of UNECE ICP Vegetation programme, systematic studies using moss were carried on in North-western Russia, and the results were presented in the European Atlas *Atmospheric Heavy Metal Deposition in Europe – Estimations Based on Moss Analysis*. In 1998–2002, JINR participated in the IAEA-coordinated research project "Biomonitoring of air pollution in the Chelyabinskregion (South Ural Mountains, Russia) through trace elements" in one of the most contaminated areas of the world experiencing strong ecological stress from trace metals and radionuclides. JINR contributed to the 2000/2001, 2005/2006, 2010/2011 European moss surveys reporting data on some areas of Central Russia and the Urals. The active moss biomonitoring (moss bag technique) was used to study air pollution in street canyons of the intensely growing megalopolis of Moscow. A combination of instrumental ENAA at the IBR-2 reactor at JINR, Dubna, and AAS at counterpart laboratories provides data on concentrations of about 40 chemical elements (**Al**, **As**, Au, Ba, Br, Ca, **Cd**, Ce, Cl, Co, **Cr**, Cs, **Cu**, Dy, Eu, **Fe**, Hf, **Hg**, I, In, La, Lu, Mg, Mn, Na, Nd,**Ni**, **Pb**, Rb, **Sb**, **S**, Sc, Se, Sm, Ta, Tb, Ti, Th, **V**, W, Yb, **Zn**), which substantially exceed the requested by the European Atlas number of elements (given in bold). Distribution of the determined elements over the sampled areas is illustrated by the contour maps produced by the Russian software package GIS-INTEGRO with raster and vector graphics. The moss technique is supposed to be used for assessing sequences of the Fukushima disaster in the Far East of Russia.

Keywords: *air pollution; moss biomonitoring; epithermal neutron activation analysis; software package GIS-INTEGRO;*

P-0100

PHOTODEGRADATION OF PHTHALATE USING MAGNETIC HYBRID MATERIALS UNDER VISIBLE LIGHT

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The semiconductor photocatalysts have been attracted attention due to the advantages of great physicochemical stability and the effective elimination of organic contaminants. In order to effectively utilize the main part of solar spectrum, the organic dye sensitization approach was used to prepare photosensitized TiO_2 which possesses visible-light activity. The dye sensitization of TiO_2 commonly adopted phthalocyanine as the sensitizer was reported to be practical and effective. However, a major drawback still occurred in the system, which was the difficulty in achieving solid-liquid separation of nano-sized photocatalysts.

In order to overcome the separation problem, the magnetic visible-light-active photocatalysts were developed in this study. The core-shell type of magnetic materials was commonly used as photocatalysts, which normally consist of the ferromagnetic core, an active layer of TiO2, and a passive film between the ferromagnetic core and the active layer. Such kinds of magnetically separable photocatalysts have been proved to effectively degrade the organics in the aqueous solution.

Dimethyl phthalate (DMP) is one of the endocrine disrupting chemicals and almost ubiquitous in the environment. Therefore, how to effectively and economically eliminate DMP from aqueous solution is an important environmental issue nowadays. Due to the lack of previous reports on the preparation for magnetically hybrid materials, in this paper, we present experimental results on physicochemical properties of resulting magnetically visible-light-active photocatalysts prepared under various CoPc loading, and evaluation of sorption properties, photocatalytic activity and stability under visible light using DMP as a model compound in this paper. The results confirmed that the synthesized magnetic hybrid CoPc/TiO2 materials were photocatalytic active under visible light region so as to effectively degrade the DMP in the aqueous solution.

Keywords: *magnetic; titania; Co-phthalocyanine; dimethyl phthalate; photocatalysis;*

P-0101

THE EFFECTS OF NICKEL ON THE MINERAL NUTRITION OF POPLAR'S CLONES AND THEIR PHYTOEXTRACTION POTENTIAL

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Poplars present ideal wood model system for testing phytoremediation of heavy metals contaminated soils as an emerging and cost-effective technology due to fact that they act as a biological filters and biomonitors. On the other hand, contamination with Ni^{2+}ions detrimentally effect biochemical and physiological processes as well as mineral nutrition in plants. Especially, due to fact that Ni^{2+} as a trace metal has same charge and similar atomic radii as some macronutrients such as Ca^{2+} and Mg^{2+}, disturbances in their transport are expected.

In this study, experimental trial was settled in greenhouse, in half-controlled conditions with three poplar clones cuttings (B229, PE 19/66 and M1) which grown and were exposed to different concentrations of Ni^{2+} (25, 50, 100 and 150 mg/kg). The aim of this study was to asses differences in poplar's clones phytoextraction potential as well as changes in mineral nutrition in poplar clones induced by nickel contaminated soil. Using atomic absorption spectrophotometry (AAS), distribution of absorbed Ni by organs (root, shoot and leaves) as well as contents of Ca and Mg were determined in poplar clones. Also, N, C and P contents were determined by elemental analysis (C,N) and spectrophotometrically (P). Gained results showed that by enhancement of applied Ni concentration in soil, accumulated Ni increased in all examined plant organs in all clones, where clone PE 19/66 showed highest phytoremediation potential among other clones by accumulating 210,12 and 143,513 ppm in roots and leaves, respectively at highest treatment. Obtained results should be used in selection of nickel tolerant poplar clone with interesting perspectives of application in phytoremediation technologies and as a platform for forestation programs of Ni polluted soils.

Keywords: *poplar; nickel; phytoextraction; mineral nutrition; phytoremediation;*

P-0102

HOW TO ESTIMATE THE PHYTOEXTRACTION POTENTIAL OF PLANTS?

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Phytoremediation describes the cleaning of polluted environments by use of plants. A special way to remediate is to extract heavy metals from soil through uptake by plants. Advantages of phytoremediation are the low costs and a high acceptance in the population. A promising phytoextraction plant is the sunflower *(Helianthus annuus)*.To test its potential under real conditions we grew sunflowers on the testfield "Gessenwiese", which is situated in the former uranium mining district of Ronneburg (Thuringia). This area is contaminated with a broad range of heavy metals such as Cd, Cr, Co, Cu, Ni, Th, U and Zn and also shows elevated values for rare earth elements (REE). The harvested sunflowers were analyzed for the above named elements in roots and above-ground plant parts. The soil was analyzed for the total content, the bioavailable fraction and the specifically adsorbed fraction (Zeien and Brümmer, 1989). Often the phytoextraction potential of a plant is estimated based on first: transfer factor (TF) - content ratio of roots vs. soil, second: translocation factor (TL) - content ratio of above-ground plant part vs. roots, and third: bioaccumulation factor (BAF) – content ratio of above-ground plant parts vs. soil. Generally, for soil the total elemental content is taken into account. To our opinion this is not satisfying, since the content determined by total digestions contain a high fraction which is not available to the plants. Because of this drawback we additionally calculated TF and BAF with the bioavailable and specifically adsorbed soil fractions. This revealed much higher TF and BAF, compared to total soil calculation, so that the sunflower can be claimed as a good metal extractor. In addition it shows, that the plants solubilize even more metals, than easy available for them, which means a high energy effort for them.

Keywords: *Phytoextraction; Transferfactor; Bioaccumulationfactor; Sunflower; Heavy metals;*

P-0103

ENVIRONMENTAL PROTECTION RISKS OF HEAVY METAL CONTAMINATED WOOD COMBUSTION.

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Numerous industrial activities polluted the environment in the past decades, whereupon heavy metals piled up in the soil in a bigger measure than the natural concentration. The soil pollution caused by means of toxic metals accelerated up since the beginning of the industrial revolution. Many sites were left behind following the industrial restructuring in Hungary, with polluted soil, therefore the utilization of these contaminated sites remained unsolved. The utilization of these sites requires the remediation of soil. The aim of our research is to select plant species that are able to decrease of the pollutant concentration of the soil by their accumulation ability and they grease the skids for energetic utilization of underutilized areas by their combustion. The heavy metal content of the biomass fuel is transferred into the combustion residues therefore it is necessary to analyze the hazards, the heavy-metal content and the treatment opportunities of these materials. The selected area in Gyöngyösoroszi was a mining area polluted with heavy metals. 5 wood species (Robinia pseudoacacia, Salix fragile, Populus tremula, Betula pendula, Pinus sylvestris, Quercus robur) were examined here. The composition of the woody materials was examined with Flame Atomic Absorption Spectrometry. The toxicity of the ashes was confirmed with leaching tests. Our studies confirmed the previous assumptions that before the energetic utilization of biomasses coming from areas polluted with heavy metals, a thorough examination is necessary concerning combustion technology and environmental protection.

Keywords: *contaminated biomass; heavy metals; combustion;*

P-0105

COMPOSITION AND SOURCES OF FINE PM IN AN INDUSTRIAL AREA: PORTO MARGHERA (ITALY)

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Industrial emissions are mainly characterized by analyzing PM, gaseous pollutants, involved in the secondary aerosol formation processes, and some hazardous air pollutants such as heavy metals, volatile organic compounds and polycyclic aromatic hydrocarbons. In this study a chemometric approach, including factor analysis and multiple linear regression analysis has been applied to PM chemical data and cluster analysis was used to process wind data. The aim was to identify the main sources of PM, their mass composition and relationship with local atmospheric circulation.

Samples have been collected in Malcontenta (Venice), a site selected in the surroundings of the industrial zone of Porto Marghera to be representative of an industrial emissive scenario being the most extended industrial area in Italy, with chemical and metallurgical works, oil-refineries, incineration and thermoelectric power plants burning coal, gas and refuse derived fuel.

About 190 $PM_{2.5}$ samples have been analyzed to be representative of different environmental conditions. Major inorganic ions and elements have been determined by ion chromatography (F^-, Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}), ICP-OES (Zn, Fe, Mn, Mg, Ca, Ti, Al) and ICP-MS (V, Ni, Cu, As, Cd, Ba, Pb).

Results from the factor analysis show 5 main sources of PM. The most important one links As, Cd, Pb, NO_3^- and NH_4^+ and represents the local contribution to PM of typical industrial markers such as As, Cd, Pb and secondary inorganic aerosol components (NO_3^-, NH_4^+). The second source includes crustal materials and correlates Al, Ca and Mg. The third source is characterized by the Ni – V –SO_4^{2-} association and identifies the fossil fuel combustion processes. The fourth source highlights a contribution from vehicular emissions linking Cu and Ba (tyre and brake abrasion) and K^+ and Cl^- (gasoline vehicle emissions). The last source is related to the marine aerosol (Na^+, Cl^-).

Keywords: *Transition metals; Arsenic; Cadmium; Lead; Ion chromatography;*

P-0106

THE MASS SIZE DISTRIBUTION OF AEROSOL IN A COASTAL SITE OF PO VALLEY (ITALY): LOCAL AND EXTERNAL ORIGINS OF ELEMENTAL COMPOSITION

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Venice (Italy) is located on the eastern border of the Po Valley, between an intensively anthropized mainland and the Adriatic Sea. EU limit values for many airborne pollutants are frequently exceeded as a consequence of peculiar weather conditions related to some orographic features, the closeness to the sea and the external transport of pollutants at continental and regional-scales. A total of 18 size-segregated aerosol samples were collected in a coastal semi-rural background site near Venice (Italy) in autumn and winter, i.e. in the most polluted period with the highest levels of airborne particulate matter. A 8-stage cascade impactor with nominal cut-points of 16, 8, 4, 2, 1, 0.5, 0.25 µm aerodynamic diameter was used, for a total of 144 samples. Samples were analyzed using the Particle Induced X-ray Emission technique for quantifying both major (Al, Si, K, Ca, Ti, Fe) and minor (V, Cr, Mn, Ni, Cu, Zn, Br) elements. A chemometric procedure was used to discriminate the weather conditions, local processes and remote contributions having an impact on aerosol chemical composition and size. Results pointed out the key role of the local atmospheric circulation on the sea-salt aerosol generation process and the accumulation effect of air mass stagnation on the pollutants emitted in the urban area. The contribution of external transports of air masses on the secondary inorganic aerosol formation was also clearly demonstrated. Finally, original and detailed information on the dimensional characteristics of particulate matter in the area and the main processes responsible for the changes in its chemical composition are also discussed.

Keywords: *Environmental chemistry; Sulfur; Chlorine; Silicon; Transition metals;*

P-0107

THE CHANGES OF POLLUTING ELEMENTS, ORGANIC CARBON AND N-P-COMPOUNDS IN THE SURFACE SEDIMENTS OF THE LAGOON OF VENICE (ITALY) BETWEEN 1980S AND 2000S

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The sediments of the Lagoon of Venice (Italy) have been the sink of various pollutants from different pathways, such as direct discharges from a variety of urban and industrial activities, runoff and seepage from the draining basin and atmospheric depositions. This study discusses the trend of polluting elements, organic carbon and nutrient species in the superficial sediments of the central lagoon from 1987 to 2003. The period was selected for having undergone significant changes in the contamination impact due to both the drop of emissions and enhanced erosion processes. Twenty five sites were sampled in the central part of the lagoon in 1987, 1993, 1998 and 2003. The trend of the analyzed elements (Al, As, Cd, Co, Cu, Fe, Hg and Zn) exhibit a moderate and roughly linear decline in concentrations from 1987 to 2003. An evident anomalous peak of chromium and nickel was found in 1998 with concentrations about 1.5–2 times greater than in the other sampling years. A lead clear decrease between 1998 and 2003 superimposed to a decreasing trend similar to the other metals was found corresponding to the ban of tetra-alkyl lead as an anti-knock additive in gasoline imposed in January 2002. Four factors staying behind the changes in the contamination of the lagoon were identified through a chemometric approach: **i**) heavy metals; **ii**) chromium and nickel; **iii**) sediment mineralogy and **iv**) eutrophication. Finally, the spatial distribution of these factors was plotted using GIS.

Keywords: *Environmental chemistry; Heavy metals; Mercury; Chromium; Lead;*

P-0108

REMOVAL OF COPPER FROM AQUEOUS SOLUTION USING SILICA FUME WITH/WITHOUT APOCARBONIC ANHYDRASE

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Water pollution is the contamination of water bodies such as lakes, rivers, oceans, and groundwater caused by human activities, which can be harmful to organisms and plants which live in these water bodies. Water pollution by toxic heavy metals through the discharge of industrial waste is a worldwide environmental problem. Since copper is a widely used material, there are many actual or potential sources of copper pollution. Although a limit of 2 mg/L was proposed by the World Health Organization as the provisional guideline value for copper content of drinking water, intake of excessively large doses of copper by man leads to severe mucosal irritation and corrosion, widespread capillary damage, hepatic and renal damage and central nervous system irritation followed by depression. Severe gastrointestinal irritation and possible necrotic changes in the liver and kidney could occur.

This study evaluates the use of silica fume waste material in the remediation of polluted heavy metal water to remove copper ions. For studying metal adsorption, 1 g of silica fume has been taken as adsorbent and then it has been suspended in 50 mL of 1 mg/mL $CuCl_2$, at pH between 3 and 11 with/without apocarbonic anhydrase and contacted batchwise in a thermostatic (t = 30 °C±0.1 °C) water-bath agitator for 1 h to enable equilibration of the sorbent and solution phases. The copper concentrations in the samples taken from the silica fume treated aqueous solutions of polluted river water and $CuCl_2$ solution with/without apocarbonic anhydrase have been determined by spectrophotometric method using 1-amino-2-hydroxy-4--naphthalenesulfonic acid. The experimental investigation results show that activated silica fume has a high level of adsorption capacity for Cu^{2+} ion. Consequently, it is concluded that the silica fume can be successfully used for the removal of the copper ions from the aqueous solutions with heavy metals.

Keywords: *Wastewater; Silica fume; Apocarbonic anhydrase; Copper removal; Aqueous solution;*

P-0109

CHEMWATER: 2050 VISION FOR A SUSTAINABLE WATER USE

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The European chemical industry is the world's top exporter and importer of chemicals with a record of €47 billion trade surplus in 2010[1].The links between the chemical industry and the water sector are multiple. The chemical sector is both, a main water consumer, it uses the 11% of the water abstracted in the continent and at the same time it is the provider of a **great number of products** employed in the treatment of drinking and waste water.

The European Commission (EC, 2007a)[2] recognized that water scarcity and droughts will constitute a major challenge for the European Union in the near future. At least 11% of the European population and 17% of its territory have been affected by water scarcity to date. Recent trends show a significant extension of water scarcity across Europe threatening to increase the € 100 billion costs and losses associated to these phenomena over the past thirty years. Furthermore, the gaining importance of upcoming industrial sectors such as white biotechnology is expected to result in higher demands for water adding on the current one. In view of this, it is clear that water sustainability is a main challenge to confront in the near future.

ChemWater is an FP7 project (NMP-2010-CSA-4-266851) that intends to coordinate European strategies on sustainable materials, processes and emerging technologies. It focuses on chemical and water sectors trying to establish synergies in the future development of both and to promote a shift in the paradigm of water from its current status of interminable commodity to a valuable raw material, what will result in an optimized industrial water management. The project looks at the European chemical industry as a provider of solutions for the whole water management cycle. Therefore this project fosters a new point of view: that of "chemistry for water" alongside the more traditional "water for chemistry".

The project brings together the WssTP and SusChem Technology Platforms as well as the networks of excellence EMH, ENMIX and ERIC. Experts from the two sectors as well as relevant professionals and stakeholders will jointly define a common long term vision that will enable a sustainable industrial water management in Europe. From that reference point, the consortium will detect the technological, legislative and social gaps to fill with research initiatives in order to achieve the 2050 Vision for ecoefficient water management.

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Keywords: *water; sustainable chemistry;*

P-0110

ADSORPTION OF HUMIC ACID ON ACID TREATED SPENT BLEACHING EARTH

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The adsorption of humic acid was studied on acid treated spent bleaching earth as functions of time,pH, initial concentration. The adsorption followed first order kinet,cs and rate constants for different initial concentrations were calculated. The Langmuir isotherm was well fit to the experimental data. The constants of this isotherm was calculated. The results indicated that the removal efficiency was influenced significantly by solution pH.

The results sugest that acid treated spent bleaching earth can be used effectively fort he removal of humic acid.

Keywords: *Spent Bleaching Earth; Adsorption of humic acid;*

P-0111

ADSORPTION OF AS (III) ON ACID TREATED SPENT BLEACHING EARTH

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Spent bleaching earth (SBE) that is a solid waste from edible oil processing industry was chosen as raw material The aim of this study is to remove arsenite ions by acid treated spent bleaching earth.The adsorption of As (III) on acid treated spent bleaching earth was studied as functions of time,pH, initial concentration and temperature. The adsorption kinetics was described by the Lagergren equation. and rate constants for different initial concentrations were calculated. Intraparticle coefficients and mass transfer coefficient were also calculated. The Langmuir and Freundlich isotherms were fitted by the adsorption data obtained. The values of Langmuir and Freundlich constants were determined. The results indicated that the removal efficiency was influenced significantly by solution pH.

The results sugest that acid treated spent bleaching earth can be used effectively for the removal of As (III).

Keywords: *Spent Bleaching Earth; Adsorption of As(III);*

P-0112

TREATMENT OF TABLE OLIVE PROCESSING WASTEWATER BY ANODIC OXIDATION

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In Mediterranean countries, olive processing industry generates wastewaters that contain pollutant compounds. In Portugal, the storage of olives in large open air tanks, filled with fresh water, to minimize olive deterioration while waiting for processing, is a common procedure. This practice yields a dark colored wastewater with high contents of organic matter, known by the negative impact on the environment. In fact, these wastewaters possess high concentration of phenols, which can be toxic to biological treatments, decreasing their efficiency. In this context, the introduction of advanced oxidation processes, in particular, the anodic oxidation with boron-doped diamond anodes, based on the oxidation of organics by the hydroxyl radical generated *in situ*, have been used with success for the degradation of biorefractory organic compounds.

The aim of this work was to study the electrochemical oxidation of table olive cleaning and storage wastewaters, using a boron-doped diamond electrode as anode. The efficiency of the process was studied under different operating conditions, namely initial organic load and current densities.

The experiments were conducted in a batch system with recirculation, using a single compartment electrochemical cell. All electrochemical experiments were conducted under galvanostatic conditions, with imposed current densities of 20 and 30 mA cm^{-2}. The decay in organic content during the assays was monitored by measurements of COD, TOC and UV-Visible absorption spectrophotometric analyses.

Although the tested wastewater is a multi-component solution, it behaves like a single organic synthetic wastewater and COD removal with time agrees very well with theoretical model proposed for a single component solution. For all initial organic load tested, the mineralization was very high.

Acknowledgements: *Financial support from Programa Operacional Regional do Centro 2007-2013 of QREN-Programa Mais Centro – FEDER for the project CENTRO-01-CT62-FEDER-002019*

Keywords: *Table Olive Processing Wastewater; Anodic oxidation; Boron-doped diamond anode;*

P-0113

IMPACT OF OPEN BURNING ON PM LEVELS AND CHEMICAL COMPOSITION

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The burning of pruning waste of olive trees in the field is a common practice in South of Italy. Since fields are usually close to densely populated areas, the emissions from biomass burning may cause seasonally increasing exposure to air pollutants. The aims of this study is the assessment of the impact of biomass burning source on the levels and chemical composition of PM10 by comparison to periods when no open fires there were.

The experiments were made in an olive trees field, where daily PM10 samples were collected by an High Volume Air Sampler for one week and in two different years. In particular daily PM10 samples were collected during three days when no open fires there were and during three days when biomasses were burned. Moreover, a second High Volume Air Sampler has been used to collect PM10 samples at a few meters from plume of a bonfire only during the hours when pruning wastes of olive trees were burned. Finally, during monitoring campaigns the numerical particles concentration and the PHAs TOT concentrations have been determined by an Optical Particles Counters and by a PHAs Analyzer, respectively. The chemical characterization of PM10 samples was performed in order to determine inorganic components such as ions and elements, Polycyclic Aromatic Hydrocarbons (PAHs) and carbonaceous fraction (OC, EC). The preliminary analysis of collected data showed the relevance of organic and inorganic tracer species for interpreting the impact of biomass burning source on PM levels. In fact high concentrations of OC, Cl, K, Pb, and PAHs, such as benzo(a)anthracene, benzo(a)pyrene, benzo(K)fluoranthene were observed. Finally, in this work will be provided the determination of enrichment factors (EF) for each one element and the evaluation of dimensional distribution patters of particles involved in biomass burning events.

Keywords: *conbustion; biomass burning; Chemical characterization;*

P-0114

OPTIMIZING SMALL WASTEWATER TREATMENT PLANTS BY MEANS OF A MOBILE MONITORING AND MODELLING SYSTEM

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Small municipal wastewater treatment plants often lack sophisticated monitoring systems while they are subject to abrupt changes. This results in inefficient operation or even unwanted environmental pollution.

An R+D project was carried out to develop a Wastewater Treatment Service Centre (WATC) (GOP-2008-1.3.1/B). The purpose was to create a complex service that collects and processes online data from wastewater treatment plants in order to provide a set of rules for early warning system and to carry out different optimization tasks based on the measurement results.

The WATC consists of three major parts: mobile laboratories with built-in online analysers for the influent and the effluent, online communication infrastructure and software package and the modelling module which is coupled with an expert system.

The mobile laboratories measure COD, ammonium, orthophosphate, nitrite and nitrate and sulphide on the influent stream and COD, ammonium, orthophosphate and nitrate regarding the effluent. Beside that pH, conductivity, temperature and turbidity are monitored on both sides and dissolved oxygen concentration in the aerated basins. The samples are provided hourly to the online communication system which provides the wastewater treatment proffessionals with immediate feedback on the measurement data. The results are used for the early warning system as well as the modelling module which is capable of optimisation tasks.

In the pilot project the chosen facility has an average hydraulic load of 2300 m^3/d. In order to maintain the nitrification the excess sludge removal rate was kept low in wintertime. While normally the plant would have satisfactory nitrification capacity the quality of the effluent decreased heavily by the end of the weekends. Using the online data simulation was carried out in order to find an optimum concerning nitrification capacity and sludge removal rate.

Acknowledgement: *The authors would like to acknowledge the financial support of the GOP-2008-1.3.1/B project.*

Keywords: *analytical methods; waste prevention;*

P-0115

DISTRIBUTION OF POLYCYCLIC AROMATIC HYDROCARBONS IN SURFACE WATER AND BED SEDIMENTS OF THE HUNGARIAN UPPER SECTION OF THE DANUBE RIVER

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The objective of this study was to investigate the concentration level and distribution of polycyclic aromatic hydrocarbons (PAHs) in surface water and bed sediments of the Hungarian upper section of the Danube River and the Moson Danube branch in the period of 2001–2010. The sampling sites were under the authority of the North Transdanubian Regional Environmental Protection, Nature Conservation and Water Management Inspectorate, designated by the Hungarian National Monitoring Programme. The measured data evaluation was supported by the Széchenyi University Main Research Direction Grant.

A total of 217 samples (water and sediments) were collected from four different sampling sites and analysed by GC/MS method for the 16 priority US EPA PAHs. The total concentrations of PAHs in water samples ranged from 25 to 1208 ng/L, which were predominated by two- and three-ring PAHs. The total concentrations of PAHs in sediments ranged from 8.3 to 1202.5 ng/g dry weight. Four-ring PAHs including fluoranthene and pyrene were the dominant species in sediment samples. A selected number of concentration ratios of specific PAH compounds were calculated to evaluate the possible sources of PAH contamination. The ratios reflected a pattern of pyrogenic input as a major source of PAHs. The results of this study add new data to the international database of the Danube River producing comparable and reliable information on water quality.

Keywords: *PAH; Danube; monitoring; surface water; sediment;*

P-0116

EFFECTS OF UV-B RADIATION AND BUTYLATED HYDROXYANISOLE (BHA) ON THE RESPONSE OF ANTIOXIDANT DEFENSE SYSTEMS IN WINTER WHEAT (TRITICUM AESTIVUM L. YILDIRIM) SEEDLINGS

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Due to thinness of the ozone layer, the world's surface has been exposed to UV-B radiation which is potentially harmful for the plant growth, development and physiology. UV radiation in plants are caused through the production of deleterious free radicals/reactive oxygen species (ROS) which leads to synthesis of some protective substances in plants. This protective antioxidant system includes enzymes such as peroxidase (POX), catalase (CAT), paraoxonase (PON) etc.; vitamins; phytochemicals; minerals and food addictives.

Butylated hydroxyanisole (BHA, 2-*tert*-Butyl-4-hydroxyanisole and 3-*tert*-butyl-4-hydroxyanisole) is a food additive and it is an aromatic organic compound. BHA has been widely used as antioxidants in the food industry. Effects of UV and butlated hydroxanisol (BHA) on the activities of antioxidant enzymes were studied on the leaves of wheat cultivars, in winter (Triticum aestivum L. Yildirim). Fifteen days old wheat seedlings were treated with UV radiation (240 nm, 3 day) before they are treated with BHA (20 °C). Supplementary UV-B radiation and UV-B+BHA significantly decreased chlorophyll and total phenol contents. The activities of enzyme extracts; polyphenol oxidase, catalase, paraoxonase and peroxidase were determined in the leaves both under normal, UV-B (<315 nm) and UV-B + BHA conditions for 4 days. The antioxidant enzymes weren't affected and showed enhanced activities in peroxidase, paraoxonase and polyphenoloxidase (except catalase in UV-B) and then BHA irradiated seedling. UV-B and then BHA-treated winter wheat seedling tries to counteract high level of reactive oxygen species that are produced under UV-B stress through the increased activities of antioxidant enzyme. It is brings into the minds that BHA try to counteract high concentrations of oxygen species produced under UV-B radiation stress through increase in UV absorbing compound and antioxidant enzymes.

Keywords: *Oxidative damage; Oxidative stress; Environmental stress; Polyphenol oxidase; Phenolic compaunds;*

P-0117

ASSOCIATION OF METALS WITH VARIOUS SEDIMENTARY PHASES IN DAM RESERVOIR

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In the present study sediment and water samples collected from Kowsar Dam reservoir in Kohkiluye and Boyerahmad province, southwest of Iran, are subjected to bulk digestion and chemical partitioning. The concentrations of Nickel, Lead, Zink, Copper, Cobalt, Cadmium, Manganese and Iron in water and bed sediment were determined by atomic absorption spectrometer. The concentrations of metals bonded to five sedimentary phases were estimated. On this basis, the proportions of natural and anthropogenic elements were calculated.

The anthropogenic portion of elements are as follows: Zn (96%)> Co (88%)> Fe (78%)> Mn (78%)> Nickel (78%)> > Copper (66%)> Lead (63%)> Cadmium (59%). The results show sediment contamination by Nickel, Cadmium and Lead, according to the world aquatic sediments and mean earth crust values. Manganese and Copper have strong association with organic matter and are of high portion of sulfide bonded ions. Cluster analysis was performed in order to assess heavy metal interactions between water and sediment. Accordingly, Nickel, Cadmium and Copper are earth-originated. Zink, Copper and Manganese are dominated by pH. All the elemental concentrations in water and sediment are correlated except for sedimental copper.

Keywords: *Anthropogenic; Lithogenous; Sediment; Trace metal;*

P-0118

INVESTIGATION OF SURFACE FUNCTIOANALITIES AND BIOSORPTIVE CHARACTERISTICS OF DIFFERENT HEAVY METALS USING GREEN MARINE MACRO ALGAE ENTEROMORPHA LINZA

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The biosorption mechanism of divalent Ni, Cd, and Pb ions from aqueous solutions using dried marine green macro algae *Enteromorpha linza* was investigated as a function of pH and contact time in a series of batch tests. The experimental data were evaluated by Langmuir isotherm model. The uptake capacity of the tested metal ions was markedly influenced from pH in the range of 2-3 and maximum rates were observed at pH 5 - 5. 5. The kinetics of the metal ions adsorption reached very rapidly to the equilibrium within 10 min of contact time. In addition to batch sorption tests, the functioanal groups on the cell wall matrix of dried green marine macro algae were revealed by potentiometric titration data and fourier-transform infrared analysis. The relative contribution of the chemical groups involved in metal biosorption such as carboxyl, amino, sulphonate was evaluated to characterize their binding mechanisms using these instrumental techniques. The density of strong and weak acidic functional groups in the biomass were found to be 0. 91 mmol/ g-biomass and 3.19 mmol/ g-biomass, respectively. In conclusion, the present work showed that the marine algae *E. linza* could be used as a potential cost-effective biosorbent for the treatment of complex wastewaters containing heavy metals.

Keywords: *biosorption; heavy metal; Ni; Cd; Pb; green marine algae; enteromorpha linza;*

P-0119

VITRIFICATION AGENTS EFFECTS ON SR TRAPPING USING NAX ZEOLITE AND BENTONITE.

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Zeolites are crystalline microporous adsorbents. As they are cationic exchangers, they have been extensively used to remove radionuclides from nuclear liquid wastes. Conventionally, zeolites containing radionuclides are vitrified at high temperatures. In this way, these noxious cations are safely occluded in the vitreous material and they can be stored for long periods until the radioactivity decays. Vitrified materials may in turn be sensitive to radiation or aging developing cracks and defects that could permit lixiviation.

This work relates to the study of the influence of two vitrification agents; Na_2CO_3 and $CaCO_3$, on the mode of strontium retention in synthetic zeolite and Algerian bentonite.The strontium considered as being one of the most dangerous elements present in the radioactive waste (half-life=30 years), requiring a sure and effective solution for its long-term adsorption and storage, by decreasing to the maximum any kind of diffusion and exchange between the environment and the trapping matrix (zeolite or bentonite).

This study allowed us, to select the appropriate vitrification agent. The textural, structural and morphological characterizations of Na_2CO_3/NaX, $CaCO_3$/NaX, and $CaCO_3$/bentonite mixtures treated at different temperatures (600–1000 °C) revealed that $CaCO_3$/NaX and $CaCO_3$/bentonite mixtures at 20/80 w/w heated at 600 °C are most adequate for the safe trapping of radioactive strontium. Furthermore, we note the formation of new phases (wollastonite, $\alpha Na_2O.2SiO_2$ + $\beta Na_2O.2SiO_2$ and quartz) even at relatively low temperatures of treatment (600 °C). These new phases permit to improve the irreversible trapping of radionuclides.

Keywords: *Strontium; Vitrification; zeolite; Bentonite;*

P-0120

THE ASSESSMENT OF NATURAL AND ARTIFICIAL RADIONUCLIDES IN RIVER BOTTOM SEDIMENTS AND SUSPENDED SOLIDS IN THE CZECH REPUBLIC IN THE PERIOD 2000–2010 USING GAMMA-SPECTROMETRIC METHOD

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The concentrations of natural radionuclides, radium-226, radium-228, and potassium-40, and the artificial radionuclide caesium-137, in river bottom sediments and suspended solids were monitored in the Czech Republic by the Czech Hydrometeorological Institute in cooperation with T. G. Masaryk Water Research Institute, Public Research Institution during the period 2000–2010. The data were used to evaluate the natural background levels of these radionuclides and the impact of human activities on the water environment. For potassium-40 in sediments, the natural background level was estimated to be 569±161 Bq/kg. To evaluate the background level for radium-226, the river sites affected by human activities (mining and processing uranium ore, coal) were eliminated from the assessment, and only river sites falling into class I were used for the analysis. The average natural background values were 47.8±24.1 Bq/kg for radium-226 and 47.2±23.9 Bq/kg for radium-228 in sediments and 87.9±45.9 Bq/kg for radium-228 and 73.4±54.1 Bq/kg for radium-226 in suspended solids. The river sediments were identified as good indicators of radioactive contamination, especially radium-226, which recorded historic contamination due to former uranium mining and milling. The radium-226 contamination rate was assessed using the ratio of radium-226 to radium-228. This ratio was used to classify sediment according to the relative contamination from the uranium industry. The residual contamination of caesium-137 due to the Chernobyl accident in 1986 was also assessed. Average value of caesium-137 was 14.0 Bq/kg in sediments and 25.0 Bq/kg in suspended solids.

Keywords: *river bottom sediments; radioactive contamination; radium-226; radium-228; caesium-137;*

P-0121

REMOVAL OF STRONTIUM AND CESIUM FROM AQUEOUS SOLUTIONS USING NATURAL RICE

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There is an increasing effort for stocking higly solube radioactive contaminants by transferring them from aqueous waste streams to solid waste forms. By doing that it is aimed to decrease the volüme of radioactive contaminants in aqueous waste streams. In this way, the high volüme aqueous streams are transferred from a high level radioactive waste into a low level radioactive waste which is much cheaper. Strontium-90 and Cesium-137 are dengerous radionuclides and the radioisotopes of these materials are produced with a high yield as a result of radioactive decay. As they have long life and high solublity, they are the primary materials in radioactive wastes. This study is done to find an alternative and efficient way to remove the radioactive wastes from aqueous waste streams. That's why adsorption method is used. It is also preferred as it provides cost reduction in waste treatment and as it is environmental friendly. To investigate the adsorption properties and characteristics of Strontium-90 and Cesium-137 natural rice as an adsorbent, radioactive tracers, G-Müller and gamma counter were used. To investigate the impact of binding on natural rice, the parameters which effect binding like concentration, time and temperature, have been checked. The results have been applied to adsorbtion isotherms and kinetics models. Besides, the thermodynamic parameters of adsorption system like ΔH^0, ΔS^0 and ΔG^0 have been examined and ΔG^0 energy has been calculated. Adsorption kinetics at different time intervals have been investigated, reaction rate and diffusion constant have been calculated. As a result, this study proves that natural rice can be used as good adsorbent to remove Strontium-90 and Cesium-137 from waste solutions.

P-0122

ADSORPTION KINETICS OF CESIUM IONS ON ROCK

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The preconcentration and separation of metal ions from the waste solutions have industrial importance and it has found many applications in nuclear industry and from the view point of environmental waste disposal. Fort his reason, there is a need for removal of metal ions from aqueous nuclear waste solutions using organic or inorganic adsorbents. The adsorption of metal ions in aqueous solution onto clay minerals is important in many areas of science and technology. These adsorption studies are needed in order to estimate rates of transport of the nuclides in the event of water penetration into and through the repository. The adsorption behaviour of cesium one of the more importent nuclides present in nuclear waste, has been extensively studied for some mineral solution systems. In this study adsorption of cesium ions on rock has been investigated using Cs-137 as tracer. The adsorption experiments were carreid out using the batch metod and initial concentrations of Cs ions ranged from 10^{-2} to 10^{-6} M. It was found that % adsorption values and distribution coefficient decreases with increasing initial Cs ion concentration. Adsorption experiments were performed as a function of shaking time at 293 K. Initially, the % adsorption of Cs ion increases rapidly, but then the process slow down. The slow adsorption may be due to the diffusion of the ions into the pores of the clays. Kinetic investigations were performed to elucidate the mechanism of adsorption of Cs^+ ions. It is seen that distribution coefficient decrease with increase the temperature. In order to predict thermodynamic behaviour of the adsorption process on rock. Thermodynamic constants ΔH^0, ΔS^0 and ΔG^0 were calculated at 293 K, 313 K, 333 K and 343 K.

P-0123

DEVELOPMENT OF RAPID DETERMINATION METHOD OF SR-90 IN ENVIRONMENTAL SAMPLES

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Determination and monitoring of ^{90}Sr (half-life 28.9 a) as one of the nuclear fission products (yields > 5%) belong among procedures to ensure and provide a radiohygienic safety. ^{90}Sr is studied for its biochemical similarity with calcium and possible consequent incorporation into human body. Main risk presents its daughter product ^{90}Y (half-life 2.67 d), which is a high energy β-emitter ($E_{\beta,max}$ = 2.28 MeV).

There are three main goals of research: environmental sample treatment, extraction of ^{90}Sr from samples and determination of ^{90}Sr. The poster mainly shows the first step of this study: the sample preparation. Moss samples from the surroundings of the NPP Temelín has been studied. For subsequent ^{90}Sr extraction each moss sample is necessary to decompose and liquidize. There are several methods to decompose organic samples. Using a traditional ways of "wet" and "dry" chemistry is one of them. These methods (incineration, leaching and evaporation) give us very good results, but they are time consuming and these processes have to be repeated for each sample a several times. Application of new decomposition methods, using by microwave digestion module, where decomposition process is enhanced by heating with microwaves, lead to the better results. However, by application of microwave digestion another problem occurs: the volume of digestion vessel allows us to decompose only limited amount of the sample. Because of a very low concentration of ^{90}Sr in environmental samples we would have to, to reach detection limit of ^{90}Sr, decompose a lot of samples.

The research shows the combination of analytical chemistry processes and microwave digestion is possibility how to eliminate problems mentioned above. The incineration and the consequent microwave digestion may lead to full decomposition of the moss sample and samples are more suitable for extraction.

Keywords: *strontium determination; microwave digestion; environmental sample;*

P-0124

STUDY OF URANIUM OXIDATION STATES IN SEDIMENTS FROM RUPRECHTOV ANALOGUE SITE

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It is important to study U oxidation states in environment to estimate radioecological impact of U and as a natural redox monitor for assessing geological objects and sites considered for radioactive waste storage. The aim of our work was to develop methodology for U oxidation state analysis in solid samples by comparing wet chemistry [1] and SR method - XANES [2]. The comparison of two different methods is needed to establish the reliability of the wet chemistry determination of the samples with low U concentration, which cannot be analysed by instrumental techniques due to lack of sufficient sensitivity. A novel wet chemical method for separating U(IV) and U(VI) from solid samples was developed, which does not alter the oxidation state of U during the separation procedure. Lignite samples collected from the sediment layer of the Ruprechtov natural analogue site (Czech Republic) were studied. Redox processes during U extraction were monitored using $^{236}U^{4+}$ and $^{236}U^{6+}$ tracers. XANES showed for both samples that bulk of U is in U(IV) state. $^{234}U/^{238}U$ activities ratio(AR) were also used to assess redox behavior in wet chemistry method. In case of considerable ^{234}U radionuclide fractionation, differences in AR can be measured depending on oxidizing or reducing environment was in the studied system. In our case, where we observed oxidizing conditions, AR in U(IV) fraction, with value - 0.4, does not change; whereas in U(VI) fraction, AR can decrease dramatically, depending on what part of U(IV) is oxidized during extraction. In U(VI) fraction AR is changing from 0.9 to 1.8 depending on experimental conditions. Results are in good agreement with samples from other regions of Ruprechtov site [3].

Keywords: *Uranium; oxidation state; analysis; wet chemistry; xanes;*

P-0125

CHARACTERIZATION AND PREPARATION OF TIO-PAN SORBENT

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The uranium separation from natural waters was studied at the Department of Nuclear Chemistry in late 80's and early 90's. TiO-PAN sorbent (titanium dioxide embedded in polyacrylonitrile) embodied high sorption capacity for uranium.

The purpose of this project was the thorough characterization of TiO-PAN sorbent with dynamic and static experiments which include kinetic experiments, sorption isotherm, effect of several ions (Ca^{2+}; Mg^{2+}; Fe^{3+}; NO_3^-; SO_4^{2-}; Cl^-; CO_3^{2-}) (V/m = 500 ml/g). It was found that CO_3^{2-}, SO_4^{2-} and NO_3^- ions have a positive effect on uranium sorption and on the other hand Cl^- ions have a negative sorption effect. Specific surface area was measured and compared with results gained in 2001.

The uranium concentrations were determined by Time Resolved Laser Induces Fluorescence Spectrometry (TRLFS) which allows us to measure uranium concentrations up to ppb level. A strong influence of Cl^- ions present in the solutions was seen, thus the calibration of TRLFS has to be made in order to determine the correct uranium concentration.

Keywords: *uranium; TiO-PAN;*

P-0126

URANIUM SORPTION AND AMS MEASUREMENTS

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The uranium separation from natural waters was studied at the Department of Nuclear Chemistry in late 80's and early 90's. TiO-PAN sorbent (titanium dioxide embedded in polyacrylonitrile) showed high sorption capacity for this element.

This composite sorbent is planned to be used for uranium preconcentration for measuring environmental ^{236}U/U ratios by Acceleration Mass Spectrometry (AMS) in bilateral cooperation with the University of Vienna. After the preliminary AMS results showing anthropogenic contamination in TiO-PAN sorbent, the preparation of titanium oxide was studied with a strong emphasis on elimination of this contamination. Several samples of titanium oxide were prepared from an organic uranium-free compound. These samples were studied using X-Ray Diffraction for their crystal structure and using selective sorption of nitrogen gas for their specific surface area. Their sorption properties were also evaluated.

Presently we are focusing on finding a water source which is not anthropogenically contaminated in order to use this water for further experiments and on the following separation and concentration steps for AMS sample preparation.

Keywords: *uranium; titanium oxide;*

P-0127

RETENTION PROCESSES OF SELENIUM SPECIES ON CZECH GRANITIC ROCK

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Selenium (Se-79, $T_{1/2} = 6.5 \cdot 10^4$yrs) belongs among fission products with long lifetime, high mobility and prevailing anionic character. Retention of selenium depends on its oxidation state therefore knowledge of migration behaviour under different conditions can significantly improve input into performance and safety assessment models.

Granite is considered as a potential host rock for deep geological disposal of radioactive waste in several countries, including Czech Republic. Considering that, retention processes of selenium species on granitic rock were investigated using sorption and diffusion experiments. Granitic rock from Melechov massive (Centre Bohemian Massive, Czech Republic) was used as a representative for crystalline rock material.

The sorption batch experiments were conducted on the crushed granite, which was sieved into several fractions with defined grain size. Mineral composition of each granitic fraction was evaluated using X-ray diffraction. The through-diffusion experiments were conducted on the granitic discs of the same origin (Melechov Massive, average 50 mm, and length 10 mm). Granitic discs were saturated with experimental tracer solution Na_2SeO_3 or Na_2SeO_4. Afterwards they were placed into diffusion cells. Due the saturation we can directly observed steady state diffusion processes.

The X-ray diffraction results showed differences in mineral composition of granitic fractions (different content of quartz, feldspar, plagioclase, mica, chlorite, kaolinite). The enrichment/depletion, namely concerning Fe containing phases (micas) can influence the extent of both sorption and diffusion of observed tracers.

Sorption experiments revealed that retention of selenite was higher then sorption of selenate. Granitic fractions enriched in mica indicated increased affinity to selenite. However, presence of mica did not influence sorption behaviour of selenate. The diffusion experiments suggested similar trend: selenite exhibited lower diffusion movement through rock samples in comparison with selenate. Selenate was proved to be rather mobile, almost non-sorbing specie.

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Keywords: *selenium; granite; retention;*

P-0128

INVESTIGATING THE CHEMISTRY OF STUDTITE

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Studtite, $[UO_2(\mu\text{-}O_2)(H_2O)_2].2H_2O$, and the dehydrated form metastudtite, $[UO_2(\mu\text{-}O_2)(H_2O)_2]$, are the only two stable mineral peroxides known. Studtite has been identified on the surface of spent nuclear fuel (SNF). The generally accepted mechanism of formation of studtite is by the reaction of UO_2 (a primary component of SNF) with H_2O_2 (generated by the α-radiolysis of water).

One of the reasons studtite has been studied in recent years is the realisation that studtite has been seen to affect the mobility of radionuclides in SNF via sorption or incorporation into the uranyl-oxygen network – something that when occurring on the surface of SNF in repositories can have great environmental repercussions.

This presentation details our investigations into the electronic properties of studtite via photochemical and cyclic voltammetric techniques and examining the redox chemistry of studtite. We also explore the reactivity of studtite with radionuclides (such as ^{241}Am) and their analogues.

Keywords: *Spent Nuclear Fuel; Nuclear Waste; Uranium; Cyclic voltammetry; Radiochemistry;*

P-0129

OCCURRENCE OF SB(V) AND SB(III) SPECIES ALONG A PH AND REDOX GRADIENT IN THE CARNOUL'S MINE WATERS (SOUTHERN FRANCE)

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The concentration and speciation of antimony were investigated along a pH and oxygen concentration gradient in the Reigous-Amous-Gardon continuum downstream from the abandoned Pb-Zn Carnoul's mine (Gard, France). Conditions of pH and dissolved oxygen concentration (DO), acquired through long-term monitoring study, ranged from acid suboxic in Reigous Creek at the outlet of sulfide tailings impoundment, to near neutral oxygenated at downstream sites along the rivers Amous and Gardon. Concentration of antimony in the fraction below 0.22 µm decreased from 7.7 - 409.9 µg L^{-1} at the source of Reigous Creek to 0.22 – 0.45 µg L^{-1} in the Gardon River. Dissolved Sb concentrations were predominant upon particulate Sb concentrations in the rivers Amous and Gardon but dissolved to particulate distribution coefficient log Kd exhibited a wide range of variations, from 2.4 L kg^{-1} to 4.9 L kg^{-1}. Speciation analysis carried out both in the fraction below 0.22 µm and below 10 kDa indicated that in the suboxic conditions of Reigous Creek water, Sb(III) represented up to 38% of total Sb in the fraction below 0.22 µm, among which colloidal Sb(III) occurred. Conversely, in the Amous and Gardon rivers, Sb(V) was the only species present in the fraction below 0.22 µm and it was not associated to the collo?dal phase. Speciation calculations allowed to identify $Sb(OH)_6^-$ and $Sb(OH)_5$ as the predominant Sb(V) species both in Reigous Creek water and in the rivers Amous and Gardon, while Sb(III) was in the form of $Sb(OH)_3$. These calculations indicated that the whole Sb(III) species did not represent as much as 6 % of total aqueous Sb concentration, which was lower than the proportion obtained from redox speciation measurements. This discrepancy was attributed to kinetic effect.

Keywords: *antimony; acid mine drainage (AMD); speciation;*

P-0130

RECLAMATION OF MINE TAILINGS USING BIOCHAR AND SEWAGE SLUDGE

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In order to make barren tailings suitable for plant growth, amendment is necessary. The possibility of using biochar, the carbon-rich product of biomass heated without access to air, in combination with aluminium and iron precipitated sewage sludge in reclamation of mine tailings is explored. The biochar used was made from CCA (copper, chromium, and arsenic) treated wood sources in a microwave pyrolysis process at <400 °C. Lack of organic matter and a subsequent poor soil structure and low water holding capacity make tailings into a hostile environment for plants. Due to its porosity, large specific surface area, and its recalcitrant behaviour in soil, it is hypnotized that bio char will act as an efficient sorbent and immobilize heavy metals. A mixture of bio char and sewage sludge, containing nutrients, organic matter and fine particles (clays and silts), is further on believed to increase soils water holding capacity as well as cation exchange capacity and thereby improve the conditions for plant growth. A pot experiment was conducted with varying mixing of mine tailings, bio char and sewage sludge and with Italian ryegrass (*Lolium multiflorum*) as test species. Sequential extractions of arsenic, copper and chromium in soil and plant material were carried out to get a clearer impression of the immediate and long-term risks of bioaccumulation. Compared with biochar, addition of sewage sludge turned out to be the more important factor determining establishment of a fertile vegetation cover on mine tailings. Sewage sludge provided a dramatic reduction in plants uptake of As and Cu compared with bio char and mine tailing only. Sequential extraction reviled high retention of Cu, Cr, and As. Speciation of As showed mostly As^{3+} in the water soluble fraction and As^{5+} in the surface bound fraction. Plants contained overall mostly As^{3+} and small amounts of As^{5+}.

Keywords: *mine tailings; reclamation; biochar; sewage sludge; metal bioavailability;*

P-0131

FOUR-YEAR CONTINUOUS MONITORING OF THE MEIRAMA PIT LAKE

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Following the technical closure of the brown lignite Meirama mine (N Spain) in April, 2008, the reclamation of the mined area started with the controlled flooding of its large pit. During the first six months of flooding, the sequential stopping of the ground water dewatering system led to the grown of an acidic water body ($pH = 3.2$; acidity = 5 meq/L; $EC_{25} = 2$ to 4 mS/cm) of about 2 hm^3 volume. Since October, 2008 the stream water of some surrounding creeks has been diverted towards the pit so that this has become the major water input in the flooding process. At the moment of writing the present abstract the Meirama lake slightly more than one half of its final volume (146 hm^3). The flooding sequence as well as the contrasting hydrochemical features of the inflowing waters has resulted in a complex evolution which has been continuously monitored during the past 4 years. The records available illustrate that the initial, acidic, water volume remains isolated from the main water body although we observe a distinct evolution connected with diffusive transport processes (where the concentration gradient is steep), the water column depletion of oxidant species and the minor input of ground water. The upper water body (accounting for approximately 97 % of the present lake volume) has chemically evolved following a path that resembles that of a mixing reactor system, where the progressive dominance of stream water and the isolation of the deep acidic water volume have induced little contrasts with respect the hydrochemistry of the stream waters. Many parameters show strong seasonal variations (rises or drops), all of them connected with peaks of biological activity that induce the steep rise of pH and the concentration of dissolved oxygen. At present, those parameters whose concentrations are regulatory prescribed comply with the corresponding water quality standards

Keywords: *pit lake; acid drainage; hydrochemistry; mine water; coal mine;*

P-0132

ASTURIAN MERCURY MINING DISTRICT(SPAIN)AND THE ENVIRONMENT: A REVIEW

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Mercury is of particular concern amongst global environmental pollutants, with contaminated sites abundant worldwide, many of which are associated with mining activities. Northwest of Spain (Asturias) can be considered a Hg metallogenic province with abundant deposits, whose paragenesis includealso As-rich minerals. Several mines have operated in this region since antiquity, with evidence of activity on individual sites since the 1st and 2nd centuries. This leaded Asturias to become an important Hg producer at the world scale during the decade 1962–1972, with average production of 15,000 flasks/year. Taking into account the losses during mining and inefficient smelting, the release of Hg and associated elements into the environment, (of which As is of particular note), was significant.As occurred in other Hg mining districts all around the world, the great decline on Hg prices on the 1970's gave rise to the closure of Asturianmines. At that time, the environmental concern was not the current one, and mines were abandoned long before the introduction of any environmental regulations to control metal release from associated spoil heaps and tailings ponds. Aninheritanceof derelict underground and surface mine facilities (shafts, galleries, and external buildings) and spoil heaps, still remains in the sites of this district. Consequently, the environment is affected globally, as high metal concentrations (mainly Hg and As) have been found in soils, waters, sediments and air,and the potential adverse health effects of the exposure to these elements, have been assessed.

P-0133

CHARACTERIZATION OF MICROALGAE ISOLATED FROM ACID MINE DRAINAGE (AMD) AS A POTENTIAL SOURCE FOR BIODIESEL PRODUCTION

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In an era of increasing oil prices and climate concerns, biodiesel has gained attention as alternative energy sources. Biodiesel derived from microalgae is a potential renewable and carbon neutral alternative to petroleum fuels. One of the most important decisions in obtaining oil from microalgae is the choice of algal species. A total of 32 microalgae cultures were isolated from an AMD (Acid Mine Drainage) in South Korea. 5 microalgae isolates were selected based on their morphology and ease of cultivation under our test conditions. The name of microalgae Nephroselmis sp. KGE 1, Nephroselmis sp. KGE 2, Uronema sp. KGE 8, Scenedesmus obiquus KGE 9 and Micractinium sp. KGE 10, based on 28S rRNA (D1D2 forward primer 5'-AGCGGAGGAAAAGAAACTA-3',D1D2 revers primer 5'- TACTAGAAGGTTCGAT TA GT C-3') sequence analyses. Nephroselmis sp. KGE 2 maximum growth of biomass concentration of 1.45±0.15 g dwt L-1 with a relatively lipid content of 20±0.5% w/w. Also, the fatty acids compositions of the studied species were mainly myristic, palmitic, palmitoleic, oleic, linoleic, g-linolenic, and linolenic acids. High concentration of oleic acid was also found in Nephroselmis sp. KGE 2, which led us to conclude that fatty acids of microalgae incubated in growth media were more effective for biodiesel production due to relatively lower saturation degree compared to the other cultures algal species. Our results suggest that Nephroselmis sp. KGE 2 can be a possible candidate species to produce oils for high quality biodiesel.

Keywords: *Microalgae; Biodiesel; Acid Mine Drainage; Oleic acid; lipid;*

P-0134

SPM AT SCHOOL: SEEING ATOMS IS THE BEST WAY TO LEARN ABOUT THEM

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Contemporary chemistry and physics frequently deal with the structure of matter at nanoscale level. One of the most important techniques used for imaging and measuring surfaces at the nanoscale (often with atomic resolution) is Scanning Probe Microscopy (SPM). SPM is an important up-and-coming technique in both academia and industry. For this reason, it should be mentioned in secondary education, at least for students with an interest in chemistry and physics.

In order to introduce SPM into secondary education, new educational materials and approaches are needed. Therefore, we have designed an excursion concept that includes an educational text, a presentation, worksheets, tests and a verified proposal of three places in the Czech Republic where it is possible to carry out the excursion. As it is quite abstract and difficult for secondary school students to comprehend how SPM works, in addition to what was mentioned above, we have suggested two demonstrations of a visual analogy for SPM.

Both of the demonstrations were carried out on various seminars arranged for secondary school physics and/or chemistry teachers (e.g. projects Heureka, Open Science, Open Science II, Project 5P, AAA science) as well as for secondary school and undergraduate students. They met with a surprisingly good response.

Furthermore we did an orientation survey using questionnaires, interviews and worksheets among chemistry teachers from Prague and their students. Quite often students claimed that seeing atoms is the best way to learn about them. Students that had only seen demonstrations expressed that they would like to have an excursion to see SPM for real. Teaching about SPM is rather difficult, as the results of our survey showed occurrence of several misconceptions, so we will also show possible ways how to avoid them.

Keywords: *Scanning probe microscopy;*

P-0135

REALIZATION OF THE COMPETENCE APPROACH IN TEACHING ORGANIC CHEMISTRY IN ENGLISH

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Today education became a crucial criterion of «knowledge society» formation which is based on the leading of intellectual product development. The Higher education of Kazakhstan is included in Bologna process. Technology integration moves from teacher-to learner-centered methodology. Being an innovation in the high education, credit-hour system concerns the individualization of teaching-learning process. Therefore the contents and the organization of students' self-directed studies are considerably changed, and their signification is enhanced.

The term «student-centered approach in education» appeared in connection to the Bologna transformation and orientation at the outcome of the teaching process. Creation of student-centered approach in education is achieved via full-weight realization of a competence-based approach. The notion competence content itself and also goals of competences development bring to necessary of creation of means of both subject and common competences control. The most optimal means of control is seen such control means as Portfolio. Material to be included in Portfolio is, as rule, defined by teacher, sometimes, by student.

The main part of a student portfolio is the student's independent/ individual work. The main part of SDS is group and individual research projects prepared in the form of presentation. Themes of group and individual projects are tightly connected with students' future specialty. The objectives of projects development, the acquired competences, and the levels of mastering of teaching material are give in terms of Blum's Taxonomy.

Such competences are the results of teaching the given part of program in Organic Chemistry; they show the individual achievements, knowledge and practical skills, acquired and presented after the successful completion of program. So, the student portfolio plays a crucial role in the assessment of student learning.

Keywords: *portfolio; Competency; innovation;*

P-0136

CINCH – COOPERATION IN EDUCATION IN NUCLEAR CHEMISTRY

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The renaissance of nuclear power is already requiring a significant increase in the number of the respective specialists, amongst others are nuclear chemists. The project Cooperation In education in Nuclear CHemistry (CINCH) aims to coordinate the current fragmented and diverse activities in Nuclear Chemistry education and training in Europe both at Ph.D. and undergraduate levels, in collaboration with Russia. The system developed should enable formation of a long-term Euratom Fission Training Scheme (EFTS) and contribute to moving the education and training in nuclear chemistry to a qualitatively new level. The work has been coordinated also with activities of ENEN association, Division of Nuclear and Radiochemistry of EuChemMS, and the training modules of EUROATOM "chemical" IPs and NOEs.

The main results of the project with the broadest impact to students, teachers, industries, and research community will be a set of compact joint modular courses in different branches of modern nuclear chemistry, an e-learning platform available for both education and training (both applicable at the Ph.D., life-long learning, and MSc. levels), and a long term sustainable strategy for nuclear chemistry education. In this presentation, examples of the structures of the courses developed will be given and other project activities will be reviewed.

Keywords: *Nuclear Chemistry; radiochemistry; education; training; e-learning;*

P-0137

INTENSIVLEHRENDES PERIODENSYSTEM DER ELEMENTE

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Chancourtois, Newlands, Olding, Meyer, Mendeleew und andere Gelehrte sind unabhängig voneinander zum Periodizität gekommen. Dabei leisteten Mendeleew und Meyer viel mehr Arbeit zur Entwicklung dieser Idee als andere Wissenschaftler und bildeten unabhängig voneinander in den Jahren 1868/69 Periodensysteme der Elemente (PSE)

Das PSE wurde von mehreren Generationen von Wissenschaftlern vervollkommnet und in 1989 von der IUPAC angenommen. Dabei ist es auffällig, dass die von der IUPAC für gültig erklärte Variante des PSE mit dem „Kopf' nach unten dargestellt ist. Aufgrund dieses Mangels der Variante kann man das Schema des Atombaus in normaler Weise nicht anbinden.

Ich habe daher eine kleine aber prinzipielle wichtige Veränderung an der derzeitig gültigen Variante PSE vorgenommen werden - das PSE wird auf die „Beine' zugestellt: die Elemente mit kleinen Kernladungen H und He stehen somit unten und die Elemente mit großer Kernladung werden aufsteigend nach oben angeordnet. Auf der linken Seite der Tabelle wird das Schema des Atombaus dargestellt. Die Stellung den Elementen in den Gruppen und Perioden ist mit dem Schema der Reihenfolge der Besetzung der Elektronen von den Haupt- und Nebenenergieniveau logisch verbunden.

Bei jedem Element sind die wichtigsten Daten (Elektronenkonfiguration, Atomradius, Elektronegativität, Oxidationszahlen, Standardpotentiale E^0 etc.)

angeführt. Die Spannungsreihe der Metalle mit E^0 von den katodischen Vorgängen ($2H^+/H_2$, $2H_2O+O_2/4OH^-$ etc.) ist auch dargestellt. Die selbstpassivierende Metalle und die Metalle, dessen Oxide und Hydrooxide amphoter sind werden bezeichnet.

Auf dem Grund dieser Daten kann man die chemischen Eigenschaften der einfachen Stoffe beschreiben, chemische Formel von den verschiedenen

Verbindungen (Hydride, Oxide, Basen, Säuren etc.) bilden und auch ihre chemische Eigenschaften sowie einfache und Redoxreaktionen beschreiben.

Also sind in dieser Variante des Periodensystems die Elemente logisch und anschaulich angeordnet und aufgebaut. Somit stimmt hier der Aufbau des PSE mit dem Atombau überein, was den Lernprozess bei Schülern und Studenten vereinfacht.

P-0138

OPPORTUNITY OF TEMPUS ?158918-AT-CANDI PROJECT FOR DEVELOPMENT OF EDUCATIONAL PROCESS IN HEES

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One of the CANDI project objectives on theme “Teaching competency and infrastructure for E-learning and retraining” is a preparation and development infrastructure for E-learning in HEEs of Central Asia with a glance of European countries experience.

At fulfilment of project the basic courses for distance education at retraining of industrial staff have been chosen, such as Inorganic chemistry, Analytical chemistry, Technology of inorganic substances, Technology of high molecular compounds. The new programs for learning in HEEs have been created. The platform Moodle have been chosen, in accordance with requirements of which the test tasks and checking questions on each lectures themes have been prepared, with account of self-study training of students. Student, selecting theme, prepares report of 10 or 20 pages, and sends this work for check and estimation. Also student participates in checking and estimation of 5 reports on given course, where he independently tries to acquire necessary knowledges for implementation this process. The program analyses some variants of estimation from different students and deduces total assessment of reports.

Program includes fulfilment of laboratory experiments. So the methodical aids for laboratory studies fulfilment have been prepared, and the video-materials have been shooted. For acquirement on the fulfilment of laboratory experiments the cheching questions and tasks have been provided.

For total assessment of course and access for exam student interview with lecturer.

For preparation materials teacher should have sufficient skills and teaching competency, which have provided in the framework of project, by participation and training in workshops on developing components of e-learning, including work with camera for video-materials. Thereby, necessary skills for preparation of developing courses have been acquired by developers, and teaching aids have been prepared.

Keywords: *Infrastructure; E-learning; teaching competency; skills; self-study training;*

P-0139

RADIOCHEMICAL TASKS DEVELOPED FOR PRACTICAL EXERCISES IN RADIOCHEMISTRY TECHNIQUES

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The Department of nuclear chemistry, FNPSE CTU in Prague founded is one of the few institutions in central Europe which provides a full Bachelor’s and Master’s degree programme in nuclear chemistry. Our department pays strong attention to the familiarization with basic techniques of instrumentation in a radiochemical laboratory. To improve practical skills of our students we are now developing new practical exercises to meet today’s requirements and fundamental knowledge for work in radiochemical laboratories. Preparations of radioactive solutions, handling of radioactive liquids, basic extraction methods, detection of ionizing radiation or surface decontamination are basic procedures students need to get acquainted with. The completion of Practical exercises in radiochemistry techniques is the first step on their way to become “nuclear chemists”. Our teachers focus on the individual access and good supervision of the students which allow to achieve a high level of comprehension to those problems. The course of Practical exercises in radiochemistry techniques is part of Bachelor’s degree programme and allows students to undertake more advanced laboratory exercises in nuclear chemistry, radioanalytic methods, detection of ionizing radiation during Master’s degree programme.

The poster shows and describes two tasks which relate to surface decontamination and solvent extraction. Simple handling, not any complex apparatus and good description make easier for students to understand a problem and give them a basic insight how to work in radiochemical laboratory.

Keywords: *practical exercise; nuclear chemistry; extraction; decontamination;*

P-0140

ISSUES OF ETHICS IN CHEMISTRY: A PERSONAL OPINION

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The relation of ethics and chemistry represents an important connection between a classical science discipline (chemistry) and more sociological and philosophical discipline (ethics). However, the connection of such disciplines was defined in early stage of science e.g. with Aristotle or Plato. In 2011, Frank et al. [1] published an interesting article related to problems of ethics in chemistry and also started discussion about this theme. In my contribution, a personal opinion on four main themes related to the ethics and chemistry will be presented. First, a short review of issues that need to be addressed will be discussed. Then probably the most important problem related to the economic profit vs. ethics issues will be addressed. Next point will be connected with experiences of ethics issues in medicine that could serve as a model for issues of ethics in chemistry. And finally, some university students' ideas on such theme will be presented with a proposal of questionnaire to evaluate their opinions.

Acknowledgement: *The financial support of my work by the Operational Program Research and Development for Innovations – European Regional Development Fund (project CZ.1.05/2.1.00/03.0058) is gratefully acknowledged.*

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Keywords: *ethics; chemistry; teaching;*

P-0141

THE NATURAL COMPOUNDS IN HIGH SCHOOL CHEMICAL EDUCATION

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Methods of learning about natural compounds have changed in recent years mainly due to their use in daily life. Saccharides, lipids, proteins and nucleic acids are found traditionally in the textbooks, other natural compounds are mentioned less. Nowadays there is emphasis on pigments, aromas, tastes, pheromones and food additives.

The Framework education programme in Czech Republic enables the variability in the chemistry education. In every high school there is its own school education program, which is specific to the school and allows teaching natural compounds in less or bigger extent.

There is a problem with laboratory works in high school due to allocation of hours. Somewhere they are not realized at all, elsewhere students have them only a few times per school year. Experiments with natural compounds are attractive, because students know the material from home or supermarket.

We are going to interpret the results of our research about natural compound in high school chemical education. We will show that natural compounds have connection with daily life and experiments with them are interesting for students.

Keywords: *Natural products; Dyes/Pigments; Pheromones; Terpenoids; Alkaloids;*

P-1015

THE ULTIMATE FRONTIER: A NEW APPROACH FOR CHEMISTRY IN A DEVELOPING COUNTRY

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As the 4th university founded in America, the University of San Carlos (USAC) has the responsibility for most of the higher education in Guatemala. Unfortunately, the role of chemistry has been mainly descriptive during the last years. The tools for education and research have been scarce and, even though education is being given and research is being made, the resources are limited. Taking this into account, some students and teachers have proposed a different approach: to promote the career in high schools, private industries and eventually make links internationally. The goal is to focus on theory. Theoretical chemistry and especially computational chemistry are branches which allow developing countries to make research at a low cost and with minimal resources. The first efforts are being made already. The First Central American Chemistry Congress made by students and professors, were students have the main role in selecting the lecturers, will be carried away next month. A special team of students is making some proposals for the renewal of the careers curriculum. And in the area of research, some projects in the field of organic synthesis, natural sea products, pharmaceutical, environmental, inorganic and supramolecular chemistry have been already carried away with promising results. Besides, some software and a small infrastructure have been acquired to take the first steps into chemical modeling and simulation. The idea is to form a theoretical chemistry group, a computational chemistry group and a high performance computing grid, based on GPU and cluster technology. The latter is thought to work between the state university and private universities in the country to support all experimental research made in Central America. In conclusion, by building a network of Central American chemists and working with other universities from other countries, especially those with the resources and tools to make the experimental part of a project, Guatemala could start making high level research and contribute with science around the world, producing results within international standards in a much more efficient and effective way.

P-1019

STUDYING RADIOCHEMISTRY BY 1930 □ BRANCA MARQUES A PORTUGUESE WOMAN CHEMIST IN THE CURIE LABORATORY

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Branca Marques (1899–1986) was one of the first Portuguese women chemists in Portugal. She graduated in Physics and Chemistry in 1925, and even before finishing her degree she was invited by the Director of the Chemistry Department to be his assistant, thus becoming the first woman teaching in this department. Fascinated by the new field of radioactivity she got a grant of the Portuguese government to work in the Curie Laboratory, firstly to get acquainted with radiochemistry techniques, in order to come back to Portugal and install a radiochemistry laboratory. After some time, by suggestion of Marie Curie with whom she worked directly and who recognized her excellent qualities as experimentalist, she asked a prorogation of her grant and continued in the Curie Laboratory preparing her PhD thesis supervised by Marie Curie, and after her death in 1934, by Henri Debierne.

In 1935, after defending her thesis titled « Nouvelles recherches sur fractionnement des sels de baryum radif?re », Branca Marques returned to Portugal, where she continued her academic career, having also succeeded in founding a Radiochemistry Laboratory mainly aimed at applied research. After her death her spoil has been conserved in the Chemistry Department of the Faculty of Sciences. In this spoil, among many other documents, there are several laboratory notebooks as well as other notebooks and spare notes and drawings of the period that she spent in Paris in the Curie Laboratory. The analysis of these documents is very interesting, as it gives some hints, not only on her work in the Laboratory, but also about safety rules and concerns, as well as bibliography consulted for her research. In this communication a brief sketch of this analysis will be presented.

Keywords: *history of science; radiochemistry;*

P-0142

SELECTIVE FLUORESCENT SENSING OF CHLORIDE IN WATER BY A CATIONIC PINCER (NCN) PLATINUM (II) COMPLEX.

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The recognition and sensing of chloride by synthetic receptors in water is a current challenge in supramolecular chemistry. We demonstrate that a luminescent platinum(II) pincer complex can be used for sensing of chloride in aqueous solution. As receptor, we employ the cyclometalated complex [Pt(NCN)(MeOH)]TfO (NCN = 1,3-bis(2-*N*-phenylbenzimidazolyl)-benzene) (**1**). The addition of chloride to a solution of **1** in DMF-water or MeCN-water (1:1 v/v) results in quenching of its fluorescence. The optical response is due to coordination of chloride to the cationic Pt complex. The spectral response can be improved by mixing **1** with a surfactant. The encapsulation of **1** inside the hydrophobic core of the surfactant micelles enhances the apparent binding constant for complexation of chloride ($logK = 4.9$), which allows to detect chloride in the micromolar concentration range. Furthermore, the micellar system displays a good selectivity for chloride over other common anions such as acetate, pyrophosphate, ect. The chemosensing system can be used for optical detection of chloride in bottled water. Crystal structures of chloro-**1**, iodo-**1** complexes and sensing studies in solution will be discussed.

Keywords: *Platinum; Fluorescent probes; Anions;*

P-0143

OCTAHEDRAL PD(II) COORDINATION AND FERROMAGNETIC ORDERING IN PALLADIUMDISULFATE

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The reaction of elemental palladium with SO_3 in sealed glass tubes at elevated temperature leads to deep-blue single crystals of $Pd(S_2O_7)$ (monoclinic, $P2_1/n$, Z = 4, $a = 502.20(1)$, $b = 1280.50(1)$, $c = 804.30(1)$ pm, $\beta = 91.409(1)°$ [1]. Surprisingly the structure shows essentially undistorted octahedral oxygen coordination for the Pd^{2+} ions realized by six monodentate $S_2O_7^{2-}$ groups. Up to now octahedral Pd^{2+} coordination by oxygen atoms has only been achieved using rigid frameworks, e.g. in $PdAs_2O_6$ [2]. The octahedral coordination of the Pd^{2+} ion (electronic d^8 configuration) leads to the paramagnetic behavior of the compound. Furthermore, at low temperature (11.7 K) even ferromagnetic coupling is observed, providing the first example of such type of magnetic behavior for a Pd(II) compound. Investigations of the thermal behavior of $Pd(S_2O_7)$ by means of DSC/TG measurements and temperature-dependent powder diffraction reveal that in a first decomposition step $PdSO_4$ forms which degrades further to PdO and finally to elemental palladium. The intermediate $PdSO_4$ can be prepared in form of red single crystals by the reaction of palladium with oleum. Contrastingly to the disulfate the palladium atoms are in square planar coordination in this compound.

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Keywords: *Palladium; magnetic properties;*

P-0144

NOVEL POLYNUCLEAR NICKEL(II)-OXO COMPLEXES STABILIZED BY HETERPOLYTUNGSTATES

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Polyoxometalates (POMs) have been found to be notably versatile inorganic compounds that are being practiced in many fields, e.g., analytical chemistry, molecular magnetism, nanotechnology, medicine, electrochemistry, photochemistry, and catalysis.[1] In order to manufacture all inorganic complexes, lacunary polyanions are being successfully used as multidentate oxo ligands to construct multinuclear magnetic materials.[2] It has been a matter of great challenge to encapsulate high nuclearity magnetic core in diamagnetic polyoxometalate shell. As part of our continuous effort to increase number of encapsulated transition metal centers in polyoxometalate, that may have interesting magnetic properties and potential application in catalysis, we have successfully made two lacunary Keggin- and Wells-Dawson type polyanions that encapsulate 5 Ni^{II} and 14 Ni^{II} centers respectively. Both the polyanions were synthesized in a simple one-pot reaction in aqueous basic media (pH 8). The Wells-Dawson based polyanion $[(Ni_{14}(H_2O)_{11}(OH)_5(PO_3(OH))_4(\alpha\text{-}P_2W_{15}O_{56})_4]^{33-}$ (**Ni_{14}**) is composed of four Ni^{II} containing $\{(P_2W_{15}O_{56})(Ni_3O_4(OH)_2\}$ sub units, a central dinuclear nickel oxo cluster and four linking phosphate groups.

Single crystal XRD reveals that Keggin based polyanion $[Ni_5(H_2O)_4(OH)_4(GeW_9O_{34})(GeW_8O_{31})]^{14-}$ (**Ni_5**) is composed of two asymmetric Keggin units, $[\beta\text{-}GeW_9O_{34}]^{10-}$ and $[\beta\text{-}GeW_8O_{31}]^{10-}$ which are connected via a five nickel(II) centers. Both componds were characterized by single-crystal X-ray diffraction, IR spectroscopy, thermogravimetric analysis, elemental analysis, electrochemistry, and magnetochemistry.

Keywords: *Nickel; Polyoxometalates; Magnesium; Polynuclear;*

P-0145

1,4-PHOSPHONIC AND PHOSPHINIC ACID CYCLEN DERIVATIVES AS LIGANDS FOR MN(II) AND GD(III) BASED MRI CONTRAST AGENTS

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Magnetic resonance imaging (MRI) is one of the none-invasive techniques of human body examination. The only disadvantage of MRI is a low resolution and specificity, therefore, MRI contrast agents (CAs) are widely used in clinical practice (approximately in 40 % of all examinations). They increase not only resolution and specificity but also efficiency of the examination. The CAs consist of paramagnetic ion (Gd(III) or Mn(II)) and strong chelator such as DOTA or DTPA.

Cyclen is basis of many derivatives which are being used, including the DOTA ligand. 1,4-phosphonic and 1,4-phosphinic acid cyclen derivatives could be a better alternative to commercially available ones. We introduced a synthetic pathway to three of these novel derivatives and determined the stability constants with metals used in CAs (Mn(II), Gd(III)) and many others using the potentiometric titrations. All ligands have higher stability constant with Mn(II) – log K_{LM} around 12, than with Ca(II) – log K_{LM} around 8, which is the closest rival for transmetallation under physiological conditions. The strongest Gd(III)-complex is formed by ligand 1,4-DO2P – log $K_{LM} = 19.15$, which is comparable to [Gd(DO3A)] – log $K_{LM} = 21.0$. Also relaxometry studies of these derivatives were performed with Mn(II) and Gd(III). The complex [Mn(1,4-DO2P)] exhibits relaxivity 2.23 $mM^{-1}\ s^{-1}$; [Mn(1,4-DO2P^{OEt})] 2.32 $mM^{-1}\ s^{-1}$, and [Mn(1,4-DO2Bn2P^{H})] 1.54 $mM^{-1}\ s^{-1}$ at 20 MHz and 25 °C. The only suitable derivative for complexation of Gd(III) is 1,4-DO2P, which forms the complex exhibiting relaxivity 6.96 $mM^{-1}\ s^{-1}$ at 20 MHz and 25 °C.

For all complexes ^{17}O NMR measurements were carried out to determine further physico-chemistry properties.

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Keywords: *Imaging agents; Manganese; Heterocycles;*

P-0146

STRUCTURAL MODIFICATIONS OF THE HETEROBIMETALLIC MN-PT THIOCYANATO COMPLEXES AND THEIR INFLUENCE ON THE MAGNETIC PROPERTIES

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Manganese complexes with tetradentate Schiff base ligands can be used for the targeted syntheses of polynuclear or polymeric coordination compounds exhibiting single molecule magnetism (SMM) or single chain magnetism (SCM). The SMM behavior originates in a combination of the high spin state of the central metal atom and uniaxial magnetic anisotropy, which both can be attributed to the Mn(III) polynuclear complexes[1–2].

This work presents synthesis and characterization of the trinuclear and polynuclear heterobimetalic complexes, which consist of the magnetically active parts involving the manganese central atom (Mn^{III}, $S=2$) coordinated by a tetradentate Schiff base (L^4 = derivatives of *N*,*N'*-bis(salicylidene)-1,2-diaminethane dianion). These parts are bridged by the diamagnetic $[Pt(SCN)_4]^{2-}$ and $[Pt(SCN)_6]^{2-}$ species: $[(solv)(L^4)Mn\{\mu_2\text{-}Pt(SCN)_4\}Mn(L^4)(solv)]$, $[(solv)(L^4)Mn\{\mu_2\text{-}Pt(SCN)_6\}Mn(L^4)(solv)]$ and $[(L^4)Mn\{\mu_2\text{-}Pt(SCN)_6\}Mn(L^4)]_n$, solv = H_2O or CH_3OH. The compounds were characterized by elemental analysis, single-crystal X-ray analysis, SQUID magnetic measurements and infrared spectroscopy.

Magnetic data indicate that either a weak antiferromagnetic or ferromagnetic exchange interaction is present in the prepared complexes depending on the type of the exchange pathway. The magnetic interactions can be realized by several different ways in general, the covalent or non-covalent pathways are discussed within the presentation.

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Keywords: *manganese complexes; antiferromagnetic interaction; ferromagnetic interaction;*

P-0147

STRUCTURAL CHARACTERIZATION OF TWO NI(II) COMPLEXES BASED ON 2-AMINOMETHYLPYRIDINE AND TETRACYANIDOMETALATE(2-) ANIONS

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As a continuation of our previous studies on molecular magnets based on Ni(II) and cyanidometallate(2-) anions[1,2] we have from the aqueous systems Ni(II)–ampy–$[M(CN)_4]^{2-}$ (ampy = 2-aminomethylpyridine, M = Ni(II) and Pd(II)) isolated and characterized two novel complexes exhibiting compositions

$[Ni(\mathit{ampy})_3][Ni(CN)_4]\cdot H_2O$ (**I**) and $[Ni(\mathit{ampy})_3][Pd(CN)_4]\cdot H_2O$ (**II**). Both crystal structures of **I** and **II** are ionic and are formed by $[Ni(\mathit{ampy})_3]^{2+}$ cations, $[M(CN)_4]^{2-}$ (M = Ni(II) and Pd(II)) anions and water molecules of crystallization. The paramagnetic Ni(II) central atoms exhibits deformed octahedral coordination with amine groups occupying fac positions in the octahedron and M atoms within the anions exhibits usual square coordination. In both **I** and **II** the hydrogen bonds of the N-H···O and O-H···N types link complex cations, complex anions and water molecules forming hydrogen bonded layers. Additionally, these hydrogen bonded layers are linked by π-π interactions forming a 3D supramolecular arrangement. The temperature variable susceptibility (2-300 K) and magnetization studies suggest the presence of weak antiferomagnetic interactions and/or single ion anisotropy.

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Keywords: *nickel(II); hydrogen bonds; cyanido complexes; magnetic properties;*

P-0148

WHAT IS THE STRUCTURAL ARRANGEMENT TO ACHIEVE HIGH IN VITRO ANTIRADICAL ACTIVITY OF CU(II) COMPLEXES INVOLVING ANTIOXIDANT KINETIN AND ITS DERIVATIVES?

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The metalloenzyme Cu, Zn-superoxide dismutase (Cu, Zn-SOD) plays a key role in the cell protection against reactive oxygen species because it catalyses the disproportionation of the superoxide radical to oxygen and hydrogen peroxide[1]. Cu, Zn-SOD whose active site contains the imidazole-bridged copper and zinc atoms[2] has become a model compound for the synthesis of low-molecular antioxidants based on Cu(II) complexes[3].

Kinetin (N6-furfuryladenine) belongs among plant growth hormones cytokinins[4]. At present, due to its significant anti-ageing effect, it has been used in medicinal cosmetics. Kinetin itself exhibits intrinsic antioxidative properties[4], thus coordinating kinetin to copper (possible synergic effect) might lead to compounds with auspicious SOD-mimic activity.

Depending on the substitution on the kinetin molecule and on the reaction conditions, nine structurally varied complexes were prepared. The polymeric $[Cu_2(\mu_3\text{-}L^n)_2(\mu_2\text{-}Ac)_2]_n$ (**1**–**3**), dimeric $[Cu_2(\mu_2\text{-}Ac)_4(HL^n)_2]$ (**4**, **5**) [5], $[Cu_2(\mu\text{-}HL^n)_4Cl_2]Cl_2$ (**6**), $[Cu_2(\mu\text{-}HL^n)_2(\mu\text{-}Cl)_2(HL^n)_2Cl_2]$ (**7**) and mononuclear $[Cu(H_2O)_2(L^n)_2(phen)]$ (**8**, **9**) complexes (HL^n=kinetin and its derivatives; phen=1,10-phenanthroline) were characterized by elemental, thermal analyses, spectroscopic methods (IR, UV-Vis), conductivity, magnetochemical measurements and single crystal X-ray analysis. *In vitro* SOD-mimic activity was tested for all the compounds, while the best result was observed for complex **7** with IC_{50}=0.71 μM (70% activity of native Cu, Zn-SOD). The influence of the various structural types of the complexes on SOD-mimic activity will be discussed.

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Keywords: *Cu(II) complexes; kinetin; in vitro antiradical activity;*

P-0149

THE KINETICS OF SILICON TETRACHLORIDE CATALITIC REDUCTION BY HYDROGEN ON NICKEL CHLORIDE

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Nowadays it pays special attention to the reaction of silicon tetrachloride reduction due to its great importance in the technological cycle of production of polycrystalline silicon,which is used,for the microelectronics industry.Modern technology for getting silicon is based on the hydrochlorination of silicon to trichlorosilane with its following separation from the gas-vapor mixture and purification from impurities and hydrogen reduction.

Besides, the method of thermal decomposition of silane is used for silicon production, which is produced by trichlorosilane disproportionation.In this way it forms from 14 to 16kg of silicon tetrachloride as a byproduct per 1kg of the receivable silicon.

Thus from the economic and environmental points of view the whole amount of processing silicon tetrachloride have to be convert into less energy-intensive raw materials,which can be used in semiconductor silicon production.The purpose of realizing such scheme is the design of closed cycle of silicon production.

In this work we studied the reduction reaction of silicon tetrachloride in the presence of a catalyst based on nickel chloride, investigated the kinetics of the process, as well as identify the order and activation energy of the reaction studied. It's found that chlorine transfer from molecule of chlorosilanes to molecule of hydrogen and hydrogen chloride formation is one of the main reactions occurring on the catalyst surface.The mechanism of the reaction is confirmed by X-ray phase and chemical analysis. A quantum-chemical modeling of the studied reactions is in a good agreement with experimental data.

The conversion of silicon tetrachloride at 250°C was obtained up to 85%.It was proved by gas chromatographic analysis of vapor-gas mixture, which is leaving the reactor with catalyst.The catalyst porosity was 60%.Thus the conversion ratio was increased from 30% to 85% with the process temperature decreeing in 4 times.These outstanding results can provide the opportunity to creati of green technology of silicon production.

Keywords: *silicon tetrachloride; catalytic reduction; nickel chloride;*

P-0150

COORDINATION OF UNSATURATED DITHIOETHERS TO CU(I) HALIDES: FROM MOLECULES TO LUMINESCENT MATERIALS

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In the context of our work on the coordination chemistry and organometallic chemistry of sulfur-rich organic ligands such as mono- and polydentate thioethers, we have recently started to use these compounds as building blocks to self-assemble coordination polymers (Metal-Organic Frameworks) of varying dimensionality incorporating the soft metal ions Cu(I), Ag(I), Au(I) and Hg(II).

We demonstrate that the reaction of aromatic and aliphatic dithioethers of type $RS-CH_2-CH=CHCH_2-SR$ and $RS-CH_2-C\Xi CCH_2-SR$ with CuX gives rise to MOFs, in which dinuclear $Cu(\mu_2-X)_2Cu$ rhomboids, tetranuclear Cu_4I_4 cubane units or hexanuclear Cu_6I_6 clusters are present. These polymetallic secondary building units (SBUs) act as connecting nodes, which are spanned by the organic dithioether ligands. We are currently investigating in detail the different parameters (metal-to-ligand ratio, solvent, lengths and rigidity of the spacer, substitution pattern of -SR), which are controlling the topologies and dimensionalities of the resulting networks. In order to correlate the temperature-dependent emissions of these strongly luminescent materials with the Cu...Cu distances within the SBUs, some X-ray diffraction studies were performed at variable temperature. The emission properties are also rationalized by means of DFT and TD-DFT calculations.

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Keywords: *Copper; Metal-organic frameworks; Luminescence; S Ligands; X-ray diffraction;*

P-0151

NEW MOLYBDENUM DINITROGEN COMPLEXES WITH MIXED ALKYL-ARYL TRIPODAL PHOSPHANE LIGANDS

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Synthetic nitrogen fixation enables the reduction of dinitrogen ligands to ammonia. The first cyclic conversion could be achieved in the Chatt cycle by protonation of bis(dinitrogen) phosphane-Mo/W complexes.[1] Our group has been involved in synthetic, spectroscopic, and theoretical investigations of Chatt type complexes in the last years.[2]

In the classic Chatt cycle the conjugated base of the acid, applied for protonation, is able to displace one of the dinitrogen ligands in the bis(dinitrogen) complex. The presence of anionic coligands leads to a disproportionation reaction at the Mo^I stage which limits the reforming of the pivotal bis(dinitrogen) complex.

Therefore, one strategy followed in our group is to occupy the *trans* position of the dinitrogen ligand in the Mo^0 complex. This has been fulfilled by the facially coordinated tripodal phosphine ligand 1,1,1-tris(diphenylphosphanylmethyl)ethane (tdppme) recently.[3] The activation of the dinitrogen ligand could be tuned by variation of the coligands bis(dimethylphosphanyl)methane (dmpm) and bis(diphenylphosphanyl)methane (dppm).

The fact that alkylphosphane donor groups provide more electron density for dinitrogen activation brought us to the approach of applying alkyl-aryl phosphane tripodal ligands to synthetic nitrogen fixation. Here we present the first dinitrogen complexes with mixed alkyl-aryl tripod ligands of the type $Me-C(CH_2PPh_2)_2(CH_2P^iPr_2)$ or $H-C(CH_2PPh_2)-(CH_2P^iPr_2)_2$. The space demanding diisopropyl phosphane groups and the usage of dmpm or dppm as coligands influence the coordination mode to the Mo^0 center.[4]

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Keywords: *Nitrogen Fixation; Molybdenum; Tripodal Phosphane Ligands;*

P-0152

BLUE PHOSPHORESCENT IRIDIUM COMPLEXES CONTAINING SUBSTITUTED 2-PHENYLPYRIDINE AND PICOLINIC ACID FOR ORGANIC LIGHT-EMITTING DIODS

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Cyclometalated phosphorescent iridium(III) complexes have been of great interest in the study of modern organic light-emitting diodes (OLEDs)[1] since color and emission efficiency were tuned by structural modification of chromophore ligands.

Herein we synthesized and characterized two blue phosphorescent iridium(III) complexes (dfpmpyCF$_3$)Ir(pic) (**1**) and (dfpmpyhCz)Ir(pic) (**2**) using two electron density modulated phenylpyridine main ligands and one picolinic acid ancillary ligand for the fabrication of OLEDs. These complexes were thermally and electrochemically stable, and showed good photoluminescence efficiency (> 15%). The –CF$_3$ substituted on the phenylpyridine-based ligand caused a hypochromic shift in the emitting spectra in compound **1** and hexylcarbazole substituted iridium(III) complex **2** exhibited energy transfer from the carbazolyl moieties to the iridium(III) core with high external quantum efficiency[2]. The studied complexes are suitable for blue phosphorescent emitters in OLEDs. The best device performance based on compound **1** demonstrated a maximum luminance (L), external quantum efficiency (EQE), luminance efficiency (LE) and power efficiency (PE) of 5750 cd/m^2, 7.53 %, 16.86 cd/A and 5.88 lm/W, respectively with Commission Internationale de L'Eclairage (CIE) coordinates of (0.17,0.40)

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Keywords: *Blue phophorescent; iridium(III) complex; OLEDs;*

P-0153

FIXATION OF NITROUS OXIDE BY CARBENES AND THE REACTIVITY OF ACTIVATED N$_2$O

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Nitrous oxide is the main ozone-depleting substance nowadays, and it is around 300 times more potent greenhouse gas then CO$_2$. In addition, N$_2$O is an appealing oxidant due to its thermodynamic potency and environmentally friendly nature (the only by product in oxygen atom transfer reactions is N$_2$).

Recently we discovered that N-heterocyclic carbenes are able to fix N$_2$O and form stable adducts.[1] This adducts could be regarded as a source of activated N$_2$O and they display unique reactivity as evidenced by different organic and organometallic transformations.[1,2]

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P-0154

MOLYBDENUM(0)-CARBONYL COMPLEXES WITH MIXED IMIDAZOL-2-YLIDENE/PHOSPHINO-HYBRID LIGANDS: WHAT ARE THE CONSEQUENCES OF SUBSTITUTING A PHOSPHINE BY A NHC GROUP?

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Since the first isolation of a free N-heterocyclic carbene (NHC) by Arduengo and co-workers in 1991[1], NHCs have become more and more popular as ligands in organometallic catalysis. In spite of the high potential of molybdenum complexes in to olefin epoxidation or nitrogen fixation, only a limited number of molybdenum complexes carrying NHCs has so far been reported.

A series of mixed NHC/phosphine ligands has been prepared which comprises the bidentate ligand $EtImEtPPh_2$[2] having one diphenylphosphinoethyl group attached to a imidazole based carbene as well as two tridentate ligands $(EtPPh_2)_2Im$ and $PPh(EtImEt)_2)$[3], [4] having two terminal diphenylphosphinoethyl groups bound to a central NHC and two terminal NHC groups bound *via* ethylene spacers to a central phosphine, respectively. Employing these ligands the new molybdenum(0) carbonyl complexes $[Mo(CO)_4(EtImEtPPh_2)]$, *fac*-$[Mo(CO)_3((EtPPh_2)_2Im)]$, and *fac*-$[Mo(CO)_3(PPh(EtIm\text{-}Et)_2)]$ were synthesized. The complexes are investigated by X-ray structure analysis, vibrational and NMR spectroscopy coupled to DFT calculations. The mixed NHC/phosphine ligands exhibit a dramatically increased σ-donor strength in comparison to their classic bi- and tridentate counterparts exclusively carrying phosphine groups such as dppp (1,3-bis(diphenylphosphino)propane) and dpepp (bis(2-diphenylphosphinoethyl)phenylphosphine). Another distinctive feature of the tridentate ligands $(EtPPh_2)_2Im$ and $PPh(EtImEt)_2$ is their propensity to coordinate in a *fac* geometry.[5]

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Keywords: *Molybdenum; Carbene ligands; Phosphane ligands; Carbonyl ligands;*

P-0155

A MULTICHROMOPHORIC DENDRIMER FOR INTRAMOLECULAR ENERGY UP-CONVERSION

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Dendrimers are repeatedly branched macromolecules with a well-defined and tree-like structure. They are ideal scaffolds to arrange multiple and different functional units within a nanobject according to a predetermined pattern. Several examples of dendrimers containing photoactive units have been investigated in the last decade and photoinduced electron and energy transfer processes have been investigated for sensing with signal amplification and light-harvesting purposes[1].

In the present work, a dendritic structure consisting of a $[Ru(bpy)_3]^{2+}$ (bpy=2,2'-bipyridine) complex as a core and four diphenylanthracene units (DPA) at the periphery. The blue emission of DPA chromophores is observed upon green-laser light excitation at 532 nm of the Ru(II) core both in fluid CH_3CN solution and in C_2H_5OH/CH_2Cl_2 1:1 (v/v) rigid matrix at 77 K.[2] To the best of our knowledge, dendrimers have never been used for this application, apart from one example reported by us,[3] based on chromophores absorbing and emitting in the UV spectral region.

This result is very important in view of a potential application of energy up-conversion in solid state device for wavelength shifting in spectroscopy.[4] By proper choice of the chromophoric units and based on previuosly reported examples in fluid solution, these dendritic systems may be applied to the sensitization of photovoltaics by harvesting the red and near infrared region of the solar spectrum.

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Keywords: *Dendrimers; Ruthenium; Supramolecular chemistry; Energy transfer; Photophysics;*

P-0156

SYNTHESIS AND CHARACTERIZATION OF ORGANOZINK LIGATED D10 METAL COMPOUNDS

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Quite recently a new family of mononuclear transition metal complexes containing organozinc ligands has been discovered by reaction of GaCp* ligated compounds $[M(GaCp^*)_n]$ (M = Mo, Ru, Rh, Ni, Pd and Pt) with $ZnMe_2$, which affords zinc rich complexes $[M(ZnR)_{2n}]$ (R = Cp*, Me) in selective Ga/Zn and Cp*/Me exchange reactions.[1] These highly coordinated complexes represent a new class of compounds bridging metal rich molecules and intermetallic phases. Also oligonuclear compounds like $[\{Mo(CO)_4\}_4(Zn)_6(\mu_2\text{-}ZnCp^*)_4]$[2], $[(RhCp^*)_6(Zn)_6(ZnCl)_{12}\mu_6\text{-}Cl][RhCp^*_2]$[3] and $[Pd_2Zn_{8-n}Ga_n(Cp^*)_5(Me)_3]$[4] (n = 2, 4) can be obtained by similar reactions. In this poster we present the synthetic pathway for this type of zinc ligated compounds by treating heteroleptic transition metal complexes such as $[(C_2H_4)_2Ni_2(\mu_2\text{-}ECp^*)_3]$ (E = Ga, Al) or $[Ni(GaCp^*)(PMe_3)_3]$ with a proper amount of $ZnMe_2$.[5] finally giving the first dinuclear and paramagnetic as well as several mononuclear compounds like $[(Cp^*Ni)\mu_2\text{-}(ZnMe)_4Ni(ZnCp^*)_2(ZnMe)_2]$ or $[Ni(ZnCp^*)(ZnMe)(PMe_3)_3]$, respectively. The extension of this concept, a comparison of the coordination geometries with Continuous Shape Measures (CShM), as well as theoretical analysis on the DFT level of theory will be discussed.

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Keywords: *organozinc; organometallic; cluster compound; zinc;*

P-0157

COORDINATION OF OLIGODENTATE N-DONOR LIGANDS TO LI+

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Ionic liquids (IL) are of great interest in current research. Due to their tunable properties, IL can be used in a wide range of applications. Our research interest is to study chemical reactions in IL in comparison with conventional molecular organic solvents. Therefore, we investigated the coordination behaviour of N-donor ligands to Li^+ and Na^+ ions.[1][2]

The coordination of the tridentate N-donor ligand 2,2':6',2"-terpyridine (terpy) to Li^+ ions in nitromethane and the ionic liquids ($[EMIM][NTf_2]$ and $[EMIM][EtSO_4]$) was investigated using ^7Li NMR spectroscopy. To determine the coordination numbers in solution, the chemical shift of the ^7Li signal was studied as a function of the added ligand concentration in reference to an external standard. The resulting plots indicate a terpy to Li^+ ratio of 2:1. The results also show a clear curvature of the graphs which indicates an equilibrium between the coordinated and free lithium ions in solution. Based on the difference between the observed NMR data and the best linear fit, the overall stability constant b_2 for the complexation of Li^+ ions by terpy in nitromethane was found to be in the range of 10^6 M^{-2}. Temperature dependent ^7Li NMR spectroscopy was carried out to obtain the enthalpy (DH°) and entropy (DS°) of the reaction.

Furthermore, the reaction between 2,6-bis(5-*tert*-butyl-1*H*-pyrazol-3-yl)pyridine and Li^+ ions was studied. This tridentate ligand shows remarkable coordination behaviour. Depending on the ligand to Li^+ ratio different species were detected in the ^7Li spectrum.

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Keywords: *N-donor ligands; Ionic liquids; coordination chemistry; nmr titration;*

P-0158

NOVEL PLATINUM(II) CHELATE COMPLEXES VIA A PYRIDINE-SULFOXIDE BASED ANCHORING FRAMEWORK: FROM MONOMERIC SPECIES TO TRINUCLEAR TRIPODAL LIGAND DERIVATIVES

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The past decade has seen remarkable progress in the development of new materials based on transition-metal ions and organic ligands, often termed as coordination polymers (*networks*) or metal organic frameworks (*MOF*s). Within this framework, the employment of square-planar platinum(II) complexes have attracted great interest due to their potential applications as photocatalysts and in a variety of photonic devices, such as light-emitting diodes, photovoltaic cells, and chemosensors, or anticancer agents.Here we will report the new synthesis of a tripodal ligand *1*,*3*,*5*-tris{[*1*-(*2*-pyridinyl)-ethenylsulfinyl]-methyl}-*2*,*4*,*6*-triethylbenzene (C_{3symm} or nonsymm), containing both a sulfinyl and a pyridine moiety, and its utilization in the coordination of square planar Pt(II) complexes, such as *cis*-[PtMe$_2$(Me$_2$SO)$_2$], and *trans*-[PtMeCl(Me$_2$SO)$_2$]. Nice crystals of the C_3 racemic mixture have been obtained and the crystal structure of the tripodal species has been solved by means of X-ray diffrattometry. With the aim of studying the coordination ability towards platinum(II) complexes of the tripodal *k*-S, *k*'-N type chelating ligand, we have thought worthwhile to synthesize a model compound, [*1*-(*2*-pyridinyl)-ethenylsulfinyl]-benzene ligand, bringing only a sulfoxide and a pyridinyl anchoring moiety, and to explore, as a preliminary study, its behavior in coordination chemistry. All the prepared species have been fully characterized by NMR spectroscopy from the connectivities in 2D-COSY and ^{13}C,^{1}H-HSQC experiments, as also predicted by molecular mechanics calculation, and by phase-sensitive NOESY spectra.

Keywords: *tripodal ligand; platinum(II) complexes; supramolecular species; coordination compounds;*

P-0159

PHASE DIAGRAMS ARE A KEY FOR NEW IDEAS IN CHEMISTRY: SYSTEM CE-AL

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In the system Ce - Al are five intermetallic compounds determined with the next thermal stability (t,C): Ce3Al 11 - 1235, CeAl 3 - 1135, CeAl 2 - 1480, CeAl - 845, Ce3Al - 655 C /1/. The number of compounds can be defined as a result at one after another filling 3p shells of the aluminium atom-acceptors with electrons from the conducting zone of the cerium atom-donors to formation virtual complete 3s2 3p6 electron configurations. But every new formed formal electron ensemble redistribute itself by take into account of the energy minimum. Therefore every electron configuration characterized its stability and its own number of bonding orbitals. The win of energy by the electrons transitions from the conducting zone of the cerium atom-donors to the aluminium atom-acceptors with formation virtual stable bonding configurations define the energy of the alloy formation and the differences of the IMC transformation temperatures. Decrease the 3s1 3p3 electron configuration stability for the IMC Ce3 Al 11 at the filling the shielding spherical 3s orbitals of the aluminium atom-acceptors to 3s2 3p3 electron configuration conditioned more low transformation temperature for the compound CeAl 3 - 1135 C. Formation from the 3s2 3p4 formal bonding configuration an 3s1(3p3d)5 stable electron ensemble with increase the spin multiplicity and number of bonding configurations define increase the melting temperature of the Laves phase CeAl 2 to 1480 C. The further filling the free 3p orbitals of the aluminium atom-acceptors with electrons to formation 3s2 3p5 and 3s2 3p6 electron configurations define the electrons ensembles energy increasing and decreasing of the CeAl and Ce3Al IMC thermal stability to 845 and 655 C correspondingly.

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P-0160

HIGHLY SELECTIVE PD-CATALYZED HECK COUPLING REACTIONS USING A PHOSPHORUS-NITROGEN CONTAINING LIGAND

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Phosphorus–nitrogen containing ligands have particular use in catalysis where it is necessary for a part of ligand to dissociate and allow an organic fragment to coordinate and undergo transformations.[1–2] They have interesting dual characteristics; they coordinate metal ions by phosphorous and/or nitrogen sites depend on the hard-soft nature of the metal ion and the same time, the nitrogen atoms act as base whenever a base is required in the reaction. Among them, 2,6-bis(diphenylphosphino)pyridine (bdppp, $(Ph_2P)_2Py$) is an unique P-N ligand with rigid and relatively large bite angle. This rigidity governs the P...N...P bite distance so that binding a metal to each donor site places the metal ions in very close proximity (about 2.6-2.8 ?). In the other hand, the rigidity of phosphine ligand is very important in selective Pd/phosphine-catalyzed cross-coupling reactions. Therefore, in continuation of our previous study on cross-coupling reactions,[3–4] we encourage to study the Pd-catalyzed heck coupling reactions.

A series of aryl bromides containing electron withdrawing and/or electron donating groups were sufficiently used for aryaltion of styrene.

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Keywords: *Heck Reaction; Cross Coupling; Palladiujm; Phosphine;*

P-0161

CYCLEN AND CROSS-BRIDGED CYCLEN DERIVATIVES TRANS-N-DISUBSTITUTED FOR COPPER(II) COMPLEXATION

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Tetraazamacrocycles such as cyclen (1,4,7,10-tetraazacyclododecane) and their *N*-functionalized derivatives continue to interest many scientists owing to their ability to form very stable metal complexes.[1] In particular, cross-bridged tetraazacycloalkanes are proton sponges and their increased structural rigidity lead to kinetically inert metal complexes, making them interesting candidates for applications such as positron emission tomography (PET) (using ^{64}Cu-labelled macrocycles) or radiotherapy (with ^{67}Cu-labelled macrocycles).[2, 3]

In this work two different types of cyclen derivatives were synthesized, with or without a cross-bridge, exploring different methylphenol-based pendant arms in search for enhanced copper(II) coordination ability. The cross-bridged cyclen derivatives were studied comparatively with the non cross-bridged ones regarding their acid-base and complexation behaviour. Copper(II) complexes were studied in solution and in solid state by a range of potentiometric, spectroscopic and crystallographic techniques.

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Keywords: *Macrocyclic ligands; Cyclen; Cross-bridged cyclen; Copper Complexes;*

P-0162

POLYOXOMETALATES MADE OF GOLD

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In recent years there has been an increasing interest in the self-assembly of polynuclear metal-oxo complexes of noble metals (e.g. Pt, Pd, Au), leading to the class of noble metal-based polyoxometalates (POMs).[1] Such discrete species have a great potential as models for the active intermediates of H_2O_2/O_2-based oxidations catalyzed by noble metal-containing materials,[2] as well as catalysts and precatalysts for different, industrially relevant processes.

Herein we report on two heteropolyaurates, $[Au^{III}_4O_4(As^{V}O_4)_4]^{8-}$[1c] and $[Au^{III}_4O_4(Se^{IV}O_3)_4]^{4-}$, which represent the only examples of POMs made of gold to date. Both POMs exhibit a tetrameric structure with four square-planar coordinated Au^{III} ions bridged by four oxo ligands and four arsenate or selenite capping groups, respectively. The polyanions were crystallized as hydrated alkali metal salts and characterized by single-crystal XRD, elemental analysis, TGA, IR as well as ESI-MS spectrometry. The aqueous solution stability of the selenite-based POM was investigated by ^{77}Se NMR spectroscopy. The facile synthetic procedure for the preparation of these polyanions based on the condensation of *in-situ* formed $[Au^{III}(OH)_4]^-$ offers a convenient way to fully inorganic, discrete gold-oxo complexes.

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Keywords: *Polyoxometalate; gold; cluster compounds; Mass spectrometry;*

P-0163

NEW BORON-CONTAINING AMINO ACIDS DERIVED FROM POLYHEDRAL BORON HYDRIDES

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Boron neutron capture therapy (BNCT) of cancer is a binary method for cancer treatment based on selective accumulation of the non-radioactive ^{10}B isotope in the cancer cells followed by their treatment with a flux of thermal neutrons[1]. One of the main requirements for BNCT is the availability of boron compounds that can be accumulated selectively in the tumor tissue at the concentrations sufficient for the intracellular nuclear reaction. In particular, amino acids and peptides can be used as molecules carrying out the targeted delivery of boron to a tumor. We prepared a wide range of new boron-containing amino acids based on different polyhedral boron hydrides. Two different approaches were used. The first one includes alkylation of sulfur derivatives of carboranes. The *closo*-carborane based amino acids $1\text{-}HOOCCH(NH_2)(CH_2)_nS\text{-}1,2\text{-}C_2B_{10}H_{11}$ were prepared by alkylation of 1-mercapto-*ortho*-carborane with the corresponding ω-alkyl diethyl *N*-acetamidomalonates followed by acidic hydrolysis and decarboxylation. The treatment of the closo-carborane based amino acids with CsF in refluxing ethanol resulted in the *nido*-carborane based aminoacids $[7\text{-}HOOCCH(NH_2)\text{-}(CH_2)_nS\text{-}7,8\text{-}C_2B_9H_{11}]^-$. Another series of the *nido*-carborane based amino acids $9\text{-}HOOCCH(NH_2)(CH_2)_nSMe\text{-}7,8\text{-}C_2B_9H_{11}$ were prepared by the alkylation of $[9\text{-}MeS\text{-}7,8\text{-}C_2B_9H_{11}]^-$. The second approach is based on disclosure of the cyclic oxonium derivatives of polyhedral boron hydride anions (BHA = *closo*-decaborate $[B_{10}H_{10}]^{2-}$, *closo*-dodecaborate $[B_{12}H_{12}]^{2-}$, cobalt bis(dicarbollide) $[3,3'\text{-}Co(1,2\text{-}C_2B_9H_{11})_2]^-$) with terminal nucleophilic centres of natural amino acids, such as tyrosine, serine, cysteine, etc. Using this approach a series of boron-containing tyrosines $[BHA\text{-}(OCH_2CH_2)_2O\text{-}4\text{-}C_6H_4CH_2CH(NH_2)COOH]^{2/1-}$ and $[BHA\text{-}O(CH_2)_4O\text{-}4\text{-}C_6H_4CH_2CH(NH_2)COOH]^{2-}$ were prepared [2, 3].

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Keywords: *Boranes; Carboranes; Amino acids; Synthetic methods;*

P-0164

NOVEL SYNTHESIS ROUTE FOR THE ATTACHMENT OF BIOLOGICAL GROUPS TO PHOTOACTIVE RUTHENIUM(II) POLYPYRIDINE COMPLEXES

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Ruthenium(II) polypyridine complexes might be promising therapeutics in the photodynamic therapy (PDT) due to their photophysical properties allowing the formation of reactive oxygen species (ROS), stability in living organisms and convenient synthetic access.[1, 2] Additionally, they are able to be taken up in cells, which was shown in the literature.[3] To provide a targeted cellular uptake predominantly in cancer cells, biocompatible groups, i.e. sugar, have been introduced into the periphery of ruthenium(II) polypyridine complexes.[4, 5]

This work presents a convenient method to connect ruthenium(II) polypyridine complexes with biocompatible groups within the CuAAC (copper(I)-catalyzed azide-alkyne cycloaddition) click reaction.

Hence Ru(bpy*)$_2$Cl$_2$ was substituted with an alkyne bearing bipyridine forming the novel complex bis(bpy*)-4-ethynyl-2,2'-bipyridine-ruthenium(II)[PF$_6$]$_2$, which was fully characterized including an x-ray structure. Furthermore the CuAAC click reaction was first performed with benzyl azide composing bis(bpy*)-4-(1-benzyl-1*H*-1,2,3-triazol-4-yl)-2,2'-bipyridine-ruthenium(II)[PF$_6$]$_2$. CuAAC was also successfully applied to attach a glucose azide onto the above mentioned bis(bpy*)-4-ethynyl-2,2'-bipyridine-ruthenium(II)[PF$_6$]$_2$ producing bis(bpy*)-4-[(2*R*,3*R*,4*S*,5*R*,6*R*)-2-(acetoxy-methyl)-6-(2-azidoethoxy)tetrahydro-2*H*-pyran-3,4,5-triyl-triacetate]-2,2'-bipyridine-ruthenium(II)[PF$_6$]$_2$.

To the best of our knowledge this is the first reported CuAAC click reaction performed on a ruthenium(II) polypyridine. This reaction route opens an attractive way to attach any biocompatible group onto appropriate ruthenium(II) polypyridine complexes.

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Keywords: *click chemistry; photochemistry; Ruthenium;*

P-0165

A CHEMICALLY UNLOCKED BINARY MOLECULAR SWITCH

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The sensing of chemical inputs using the modulation lanthanide luminescence as an output was first achieved by De Silva[1] and has been followed by extensive work in this area aimed at producing practicable devices. The advantages of lanthanide chelate luminescence in this area are well known, constituting in many ways the optimum light-based sensors. They have been proven at analyte concentrations as low as 10^{-15} M due to their high signal to noise ratio.[2] The simplest chemical input is that of H^+ ion concentration (or pH) and this is one probably the most widely utilised to date in such molecular devices.[3] This presentation will describes a terbium macrocycle that displays extremely sensitive pH-dependent luminescence, conditional on its previous pH.

The novel organic ligand reported here is formed by the conjugation of the well-known macrocyclic moiety DO3A to a phthalimide chromophore via a propyl-bridge. In this work we found that a Tb^{3+} complex of the initial ligand can be activated by changes in pH and this active form displays luminescence that can be reversibly switched on and off by further changes in pH.

The active complex is highly luminescent with a quantum yield of 47% and an extremely long luminescence lifetime of 2.26 ms. In addition, it acts an extremely sensitive, reversible, H^+ sensor or switch between pH values of 2 and 4: the complex loses 60% of its luminescence within one pH unit.

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Keywords: *Terbium Complexes; Luminescence; Molecular Switches; Molecular Logic Gates;*

P-0166

KINETIC STUDIES OF LN(III) COMPLEXES OF DOTP-LIKE MACROCYCLIC LIGANDS

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The Ln(III) complexes of macrocyclic ligands (mostly DOTA/DOTP derivatives) are often employed in medicinal chemistry as MRI agents and luminescent probes. For any biomedical applications, these metal complexes should exhibit a high thermodynamic stability as well as kinetic inertness under physiological conditions and therefore, knowledge of their thermodynamic/kinetic properties (*e.g.* dissociation rate constants for an estimation of kinetic inertness) is important to evaluate their use in these applications.

In this work, the formation/acid-assisted dissociation kinetics of chosen Ln(III) (Ln = Ce, Eu) complexes with DOTP-like macrocyclic ligands (H_8dotp = 1, 4, 7, 10 – tetraaza-cyclododecane – 1, 4, 7, 10 – tetrakis(methylphosphonic acid) and their analogs: H_4dotp^{OEt} = tetrakis(monoethylester), H_4dotp^{H} = tetrakis(methylphosphinate), H_4dotp^{Ph} = tetrakis[methyl (phenyl)phosphinate) was studied using molecular absorption spectroscopy in UV region and time-resolved laser-induced fluorescence spectroscopy (TRLIFS). The impact of the coordination number of Ln(III) ion (Ce vs. Eu) and the softness/hardness of pendant arms of studied macrocyclic ligands on kinetic properties of Ln(III) complexes was investigated in order to optimize the structural design for synthesis of bifunctional chelators for potential medical applications.

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Keywords: *Macrocycles; Lanthanides; Kinetics;*

P-0167

PHOTOCATALYTIC WATER REDUCTION WITH RUTHENIUM POLYPYRIDYL CHROMOPHORES

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The splitting of water by solar energy, using ruthenium polypyridyl complexes can be divided into two half reactions; (**i**) water oxidation, to yield O_2 and (**ii**) water reduction, producing H_2, an alternative fuel. Systems for both separated reactions are well-known using a multiplicity of different dyes and sacrificial redox reagents. For the light driven overall water splitting both reactions must have the ability to work parallel, i.e. H_2 evolution in the presence of O_2. This could not be obtained till now. A supramolecular photocatalytic system for the water reduction consisting of a ruthenium complex with a 4,4'-dicyano-2,2'-bipyridine ligand as photosensitizer has been studied.

Surprisingly this system shows a superior catalytic activity under aerobic than under anaerobic conditions. The mechanism of this reaction was studied in detail whereby a conversion of the nitrile groups and efficient photocatalytic consumption of O_2 could be observed. Based on these results we synthesized and characterized the related ruthenium complex with a 4,7-dicyano-1,10-phenanthroline and a 4-cyano-1,10-phenanthroline ligand for comparison.

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Keywords: *Ruthenium; Water splitting; Homogeneous catalysis; Cobalt;*

P-0168

SUBSTITUTED FISCHER CARBENE COMPLEXES OF TUNGSTEN(0)

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Fischer carbenes have a wide range of applications in organic synthesis. It is also known that modification of the ligand sphere will alter the reactivity of these complexes.[1, 2] These complexes are, however, not known to be metathesis active on their own, and require activation or co-catalysts.[3] Tungsten, however, is described as a metathesis-active metal, and examples of complexes which are useful for olefin metathesis and polymerisation of unsaturated compounds are known.[4]

Phosphine and amino derivatives of tungsten Fischer carbenes were thus synthesised in order to study the effects of these changes on the catalytic activity. Theoretical studies of these complexes were also done to investigate the correlation between the distribution of the HOMO and LUMO with the activity of the molecule. Furyl- or thienyl-ethoxy tungsten Fischer carbenes were synthesised as the starting material and from there modifications to the ligand sphere were made. PPh_3 and DPPE were used as the mono and diphosphine ligands respectively. Both the cis and trans isomers were isolated for $P(Ph)_3$, while only the *mer* isomer was isolated for the DPPE derivative. Aminolysis products of the complexes were also synthesised by reacting the ethoxy carbene with cyclohexylamine.

For further comparison, an ethylene diamine aminolysis chelate was synthesised to analyse the combined effect of nitrogen on the ligand sphere and the carbene. Preliminary catalytic studies were done on the selected products.

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Keywords: *Carbenes; P ligand; Tungsten;*

P-0169

A WELL-KNOWN REACTION IN A NEW MEDIUM: THE CLASSIC “BROWN RING” REACTION IN AN IONIC LIQUID

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The properties of ionic liquids (ILs) and their advantages/disadvantages are presently discussed extensively in terms of different kinds of possible applications.[1] It is well-known that ILs in general greatly improve the solubility of gases, which could have an important effect on their activation. However, there is no sufficient information presently available on the role of the ILs in such reactions.

The present goal of our work was to study the activation of small molecules, such as NO, by transition metal complexes in ILs. The reaction of nitric oxide (NO) with transition metal ions plays an important role in environmental and biological processes.[2]

We report here detailed mechanistic studies on the reversible binding of NO to $FeCl_2$ dissolved in the ionic liquid [emim][dca], 1-ethyl-3-methylimidazolium dicyanamide, as solvent.[3] The kinetic data and activation parameters were measured using a laser flash photolysis technique at ambient and high pressure for the first time in an ionic liquid. These data suggest that the reaction follows a limiting dissociative (D) ligand substitution mechanism in contrast to occurrences in aqueous solution, where an interchange dissociative (I_d) ligand substitution mechanism was found. The observed difference apparently arises from the participation of the ionic liquid anion as N-donor ligand, as verified by X-ray crystallography. In addition, Mössbauer and EPR spectra were recorded for the reaction product formed in the ionic liquid, and the parameters closely resemble those of the $\{FeNO\}^7$ unit in other well-characterized nitrosyl complexes.

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Keywords: *ionic liquids; kinetics; nitrogen oxides; transition metals; UV/Vis spectroscopy;*

P-0170

DIMANGANESE DODECACARBONYL AND ITS LIGHT TRIGGERED CO RELEASE FROM NANOFIBROUS MATERIALS

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Dimanganese dodecacarbonyl ($Mn_2(CO)_{10}$) can release biologically relevant carbon monoxide during irradiation with light.[1,2]

Here, $Mn_2(CO)_{10}$ has been non-covalently embedded into a poly(L-lactide-*co*-D/L-lactide) matrix via the electrospinning process forming a hybrid non-woven.[3] The incorporation enables water-insoluble $Mn_2(CO)_{10}$ to become accessible to the aqueous phase. Furthermore, degradations products from the irradiation process will be retained in the polymeric matrix and therefore physiologically toxic side reactions are suppressed.[4, 5]

The nanofibrous hybrid material was characterized with FTIR, ^{13}C-NMR, UV-Vis, BET surface area measurement, DSC and SEM. Leaching of the dimanganese dodecacarbonyl from the non-woven was negligible as proven by UV-Vis and AAS. The cytotoxicity of the fibrous web was determined in a typical cell test. Irradiation experiments at 366 nm in water, using the myoglobin assay for polymeric materials, showed a significant photo-triggered CO release from the non-woven.[4]

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Keywords: *Manganese; Drug delivery; Nanostructures; Polymers;*

P-0171

SYNTHESIS OF “BUTTERFLY-LIKE” POLYPHOSPHORUS DICATIONS $[L_2P_4]^{2+}$ (L = PH_3AS, PH_3P)

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Several homoatomic cage compounds of Group 15 elements are known, and anionic and neutral derivatives of P_4 such as Zintl-anions and polyphosphanes have been developed.[1, 2] However, analogous cationic polyphosphorus derivatives have not been reported.[3] Therefore, we developed the synthesis of the “butterfly-like” polyphosphorus dication $[L_2P_4]^{2+}$ (L = Ph_3As) as tetrachloroaluminate salt $[(Ph_3As)_2P_4][AlCl_4]_2$ and investigated the reaction of this cation with different Lewis bases.[4] Thus, we could show that the Ph_3As-moieties can easily be substituted by stronger Lewis bases (L = Ph_3P, NHC) and, therefore, dications $[L_2P_4]^{2+}$ can be considered as a $[P_4]^{2+}$ synthon.

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Keywords: *Cations; Phosphorus; Cage compounds; Pnicogens;*

P-0172

CONCEPTS FOR THE IMPLEMENTATION OF FULLERENES IN SUPRAMOLECULAR PHOTOCATALYSTS

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The photocatalytic splitting of water is an intensively studied reaction, since a transformation of the sunlight's energy into chemical energy seems to be possible. Studies on this research topic revealed that supramolecular photocatalysts consisting of a photocenter, a bridging ligand and a catalytic center are of great importance to the development of photoelectric cells.[1] One of the most important factors of the activity this photocatalysts is the electron transfer from the photocenter to the bridging ligand and further the catalytic center. Supramolecular photocatalysts based on tetrapyridophenazine as bridging ligand show an ultrafast photoinduced electron transfer of one electron.[2] Water reduction requires two electrons to form hydrogen. Therefore a bridging ligand that is able to store two electrons and submit them to the catalytic center should increase the activity of the catalytic systems.

Here, we present the supramolecular interaction between the complex $[(tbbpy)_2(tpphz)Ru](PF_6)_2$ and the multi electron storage C_{60}. The occurring π-π-stacking interaction between the tpphz ligand and the fullerene was observed via ^{1}H-NMR-, UV/Vis- and Emission spectroscopy. ^{1}H-NMR analyses showed different types of π-π-interactions between the complex and the C_{60}. The presence of the fullerene heavily influences the spectroscopic properties of the complex. The energy level of the ^{3}MLCT-state of the Ruthenium complex gets lowered and its Emission gets quenched.

Moreover we present a new Bis-*tert*-butylbipyridine Ruthenium-C_{60} complex. Thereby the fullerene is functionalized with a 2,3-dimethylpyrazino[2,3-*f*][1,10]phenanthrolyl group[3] coordinating to the Ruthenium center. This complex was analyzed via UV/Vis- and Emission spectroscopy. The comparison with $[(tbbpy)_2(tpphz)Ru](PF_6)_2$ showed a higher intensity of the ^{1}MLCT band and a significant quenching of the Emission of the ^{3}MLCT.

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Keywords: *Fullerenes; Ruthenium; Supramolecular Chemistry; Photochemistry;*

P-0173

TOWARD THE DEVELOPMENT OF A SUSTAINABLE ELECTROCHEMICAL REDUCTION PROCESS OF TRIPHENYLPHOSPHANE OXIDE

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Recycling of tertiary phosphane oxide as wastes from industrial processes[1] has become an important aim in the context of sustainable use of valuable phosphorus compounds. As an example, the production of vitamin A, which key step is a Wittig-reaction, produce large quantities of triphenylphosphane oxide (TPPO) as waste in stoichiometric amounts.[2] The wasteful synthesis of the corresponding phosphanes from valuable phosphorus sources is a driving force in the exploration of the follow-up chemistry of phosphane oxides for decades.[3] We have investigated new routes to phopshane oxide functionalization and have found, that they can qunatitatively converted to pyrazolylphosphonium triflates by our recently developed compound $[pyr_3P_2][OTf]_3$ (pyr = 1,3-dimethylpyrazole).[4] The obtained pyrazolylphosphonium salts are used in a multitude of follow-up reactions to generate usefull compounds.[5]

The electrochemical reduction of pyrazolylphosphonium triflates to the corresponding phosphanes would open up an interesting aspect in phosphane oxide recycling. We inverstigated this reaction by the use of cyclic voltammetry (CV). A preparative approach under galvanostatic conditions was developed by coupling of electrolysis with *in-situ*monitoring of the pyrazolylphosphonium salt and triphenylphosphane (TPP) concentration by CV. Coulometric measurements during the CV-monitored electrolysis give further insights for a plausible mechanism. The combination of these methods enables to further optimize the electrochemical conditions to develop a waste-free electrochemical reduction process for the synthesis of triphenylphosphane from TPPO.

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Keywords: *Phosphanes; Oxides; Electrochemistry; Reduction; Sustainable Chemistry;*

P-0174

COORDINATION CHEMISTRY OF 2,6-DIPHOSPHONYLPHENYL-SUBSTITUTED DIPHENYLPHOSPHANE CHALCOGENIDES

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E,C,E-coordinating pincer-type ligands (E=heteroatoms such as N, P, O, S...) are well established for stabilizing numerous complexes of metals such as tin, platinum and palladium.[1] Beside that ability however, the coordination chemistry of the ligands themselves is not well explored. In continuation of our systematic studies on phosphorus-containing O,C,O-coordinating pincer-type ligand[2] 4-*t*-Bu-2,6-$[P(O)(Oi\text{-}Pr)_2]_2C_6H_2^-$ we present here the phosphorus-substituted derivatives 4-*t*-Bu-2,6-$[P(O)(Oi\text{-}Pr)_2]_2C_6H_2P(E)Ph_2$ (E=O, S, Se, lone pair) and complexes with a variety of transition metals.

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Keywords: *Phosphane ligands; Coordination modes; Transition metals;*

P-0175

EFFECTS OF THE PREPARATION CONDITIONS IN THE PROPERTIES OF THE $LI_{3X}LA_{2/3-X}TIO_3$ AS ELECTROLYTE IN SOLID-STATE LITHIUM-ION BATTERIES

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In recent years, all solid state lithium ion batteries have been attracting more attention owing to their properties of high power density and good safety. As an important part of the battery, inorganic solid state electrolytes ($Li_{3x}La_{2/3-x}TiO_3$, LLTO) become a significant issue because they present the highest lithium ion electrical conductivity at room temperature (about 10^{-3} S.cm^{-1} for x=0.3).[1, 2]

It is well known that the conductivity of LLTO strongly depends on the exact conditions of sample preparation. Until now most of inorganic solid-state electrolytes have been obtained by solid state reaction. As known, this conventional preparation method needs high sintering temperature and long sintering time,[3] which result in serious lithium loss during sintering process and in a particle size increase that is negative for micro-electrolyte layers in battery applications. As alternatives, some other synthetic methods have been used to prepare LLTO ceramics pellets or thin films.[4, 5] Furthermore the lithium content (x value) and the cooling rate in the sample syntesis play a crucial role in the structural properties, and then, in the materials properties as conductivity.[2]

In this sense, this study is focused on the synthesis route, sintering temperature, cooling rate and crystal stability of the $Li_{3x}La_{2/3-x}TiO_3$ electrolyte in order to find out a suitable processing conditions to use in Lithium-ion battery systems.

Keywords: *synthesis route; solid electrolyte; lithium battery; perovskite;*

P-0176

PHOTOINDUCED CATALYTIC WATER REDUCTION TO HYDROGEN BY NEW COBALT COMPLEXES BASED ON TETRA- AND PENTADENTATE NITROGENATE LIGANDS

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Currently, one of the most appealing research areas is the discovery and study of new electro- or photo-chemical catalysts based on earth-abundant elements able to generate fast and efficiently H_2 from the reduction of water.[1] Remarkable example of electro- and photochemical water reduction catalysts has been shown recently.[2] Nevertheless, regardless of the fast development of the field, only few examples of well-defined, water and oxygen robust catalysts have been developed.[3]

With this aim, we become interested in the development of well-defined, robust and modular homogeneous catalytic systems which their electronic and steric properties were easily tunable.

Hence, we presented a new family of catalysts for water reduction based on iron, nickel and cobalt complexes with robust tetra- and pentadentate nitrogenate ligands derivates from the basic 1,4,7-triazacyclononane structure. Preliminary studies show that not only all cobalt complexes[4] are active photo-induced catalysts but also the H_2 formation activity and efficiency may be modulated by the electron-drawing properties of the ligand achieving up to 420 TON in less than an hour.

In this contribution the catalytic efficiency versus the photosensitizers used such as Ir, Ru or organic dyes and sacrificial electron donors such as Et_3N, TEOA or ascorbic acid will be discussed. Finally, key intermediates will the postulated based on ongoing mechanistic studies.

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Keywords: *water reduction; hydrogen; cobalt; water splitting;*

P-0177

REACTIVITY OF DINUCLEAR PT(II) COMPLEXES CONTAINING BIDENTATE N,N- AND N,S-DONOR LIGANDS

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The cytostatic activity of *cis*-diamminedichloroplatium(II) – cisplatin – was discovered in 1969 by Barnett Rosenberg and this development marked a turning point in the treatment of cancer. However, there are a number of problems that need to be considered using cisplatin, viz. there are numerous side effects, the anti-tumor activity is limited to certain types of cancer, and some tumors develop a resistance during the therapy.

Besides new mononuclear complexes with improved properties (carboplatin and oxaliplatin), a new class of multinuclear Pt(II) complexes has been developed by Farrell and his group.[1]

We have now synthesized a series of dinuclear Pt(II) complexes in our group in which the two Pt(II) centers are connected by an aliphatic chain of variable length. Furthermore, a chelating ligand system was used that contain either exclusively N-donor atoms (NNpy) or a mixed N- and S-donor system (NSpy). These chelating systems stabilize the complex toward further nucleophilic attack and inhibit the decomposition of the dinuclear system.[2]

Cytostatic active platinum compounds react in the cell with DNA as well as with sulfur containing substances, which leads to loss of cytostatic activity. In our studies we focused on kinetic measurements to examine substitution reactions with thiourea as a strong sulfur nucleophile to gain a closer look into the reactivity of these complexes. The rate constants of substitution can then be compared for the two systems and amongst each other as a function of chain length. A detailed discussion of our latest results will be presented.[3]

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Keywords: *platinum; cytotoxicity; kinetics; reaction mechanisms; ligand effects;*

P-0178

SYNTHESIS, CHARACTERIZATION AND ANTIMICROBIAL ACTIVITY OF PALLADIUM(II) COMPLEXES WITH SOME ALKYL ESTERS OF (S,S)-ETHYLENEDIAMINE-N,N'-DI-2-(3-METHYL)--BUTANOIC ACID

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Numerous complexes based on palladium(II) ion have been synthesized and their different biological activities have been documented [1–2]. The impact of different palladium complexes on the growth and metabolism of various groups of microorganisms has been studied. Garoufis reviewed numerous scientific papers on antiviral, antibacterial and antifungal activity of palladium(II) complexes with different types of ligands [3].

Palladium(II) complexes with R_2-*S,S*-eddp ligands (*S,S*-eddp=(*S,S*)-ethylenediamine-*N,N'*-di-2-propanoate; R=*n*-pr, *n*-bu, *n*-pe [4] were synthesized and characterized.

Three new ligand precursors and their palladium(II) complexes of general formula [PdCl{(*S,S*)-(R)eddv}] (R=*n*-propyl, *n*-butyl and *n*-pentyl; *S,S*-eddv=(*S,S*)-ethylenediamine-*N,N'*-di-2-(3-methyl)-butanoate) have been synthesized and characterized by microanalysis, infrared, ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry. *In vitro* antimicrobial activity for these ligands and complexes is investigated. Testing is preformed by microdilution method and minimum inhibitory concentration (MIC) and minimum microbicidal concentration (MMC) have been determined. Testing is conducted against 15 microorganisms (five strains of pathogenic bacteria, three species of probiotic bacteria, two yeast species and five pathogenic fungi). Tested ligands, with a few exceptions, show very low antimicrobial activity. Palladium(II) complexes show selective and moderate activity. The difference in antimicrobial activity between ligands and corresponding palladium(II) complexes is noticed and it is always higher with palladium(II) complexes.

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Keywords: *Palladium; N ligands; Antifungal agents;*

P-0179

NOVEL DIETHANOLAMINE DERIVATIVES OF ANTIMONY AND BISMUTH- SYNTHESIS AND STRUCTURES

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In analogy to the 5-aza-2,8-dioxa-1-stanna(III)bicyclo[3.3.0$^{1.5}$]octanes known as intermediates for the synthesis [1] of non-toxic catalysts for polyurethane formation[2], 5-aza-2,8-dioxa-1-stiba(III)bicyclo[3.3.0$^{1.5}$]octanes of the type $XSb(OCR_2CH_2)_2NR'$(R=H, Me, R'= alkyl, aryl, X=Cl, F, N_3)[3] and new pseudostibatranes were synthesized. The latter compound shows an intramolecular MeO?Sb interaction at a O-Sb distance of 3.12 ?. The antimony salt $\{[Sb(OCMe_2CH_2)_2NMe]GaCl_4\}_2$, which is isoelectronic to the 5-aza-2,8-dioxa-1-stanna(III)bicyclo[3.3.0$^{1.5}$]octanes mentioned above, shows a dimeric structure. The 5-aza-2,8-dioxa-1--bismuta(III)bicyclo[3.3.0$^{1.5}$]octanes are dimeric structures in the solid state. The interaction of compound **2** with moisture provided a partial hydrolysis product that shows an interesting structure with two bismuth atoms.

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Keywords: *Diethanolamines; Antimony; Bismuth; Catalysis;*

P-0180

VALENCE TAUTOMERIC QUINONOID COBALT COMPLEXES WITH PHOTOACTIVE CIS-TRANS ISOMERIZABLE LIGANDS

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The recently proposed *ligand-driven light-induced spin change* (LD-LISC) is one possible approach to achieve magnetic bistability at room temperature. It is based on the possibility to reversibly change the ligand field of a transition metal complex by photoisomerization of the ligands to such an extent, that the metal ion undergoes a spin transition.[1] In this contribution we adopt the LD-LISC concept to the well explored valence tautomeric quinonoid transition metal complexes [2] which are known to exhibit different optical, electronic and/or most importantly magnetic properties due to a reversible interconversion between their electronic isomers.

Well studied 4-phenylazopyridine (4-papy) and 4-styrylpyridine (4-stpy), which undergo a reversible *cis-trans* isomerisation upon irradiation, are incorporated into a redox active Co(3,5-DBTSQ)(3,5-DBTCat) framework as photoactive ligands, where 3,5-DBTSQ$^-$ and 3,5-DBTCat^{2-} are the semiquinonate and catecholate forms of 3,5-di-*tert*-butyl-*o*-benzoquinone, respectively.

As confirmed by EPR spectroscopy in frozen solution at 14 K, the electronic structure of complexes [Co(3,5-DBTSQ)(3,5-DBTCat)(4-papy)$_2$] **1** and [Co(3,5-DBTSQ)(3,5-DBTCat)(4-stpy)$_2$] **2** consists of a ligand π-radical attached to a low-spin Co(III) ion. Cyclic voltammogram of **1** at RT reveals several typical (partially) reversible redox processes. Magnetochemical data of **1** in solid state shows a low-spin Co(III) electronic structure at T < 240 K; however, the observed gradual increase of the effective magnetic moment at higher temperatures may indicate a thermally induced transition to a high-spin Co(II) state. Upon irradiation with UV light at RT in solution a *trans*-to-*cis* isomerization of the photoactive ligands both in **1** and **2** is suggested by electronic absorption spectroscopy.

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Keywords: *Cobalt; Valence isomerization; Spin crossover; Magnetic properties; UV/Vis spectroscopy;*

P-0181

COMPARISON OF C-H HYDROGEN ATOM TRANSFER REACTIONS MEDIATED BY MANGANESE(IV)-OXO COMPLEXES WITH TUNED ELECTRONIC PROPERTIES

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Oxidation of C-H bonds mediated by transition metal complexes are fundamental steps in fine and industrial chemistry, and in many biochemical transformations. One of the most commonly metal used is iron, usually adopting high valent iron(IV)-oxo species.[1] The comparison of manganese systems with their iron analogues have also attracted the attention of different authors, trying to shed light into the Fe/Mn duality found in nature. It is known that there are some oxidative enzymes that can be both iron and manganese dependent. While several high-valent iron complexes are currently known, this is not the case for the manganese metal, for which mononuclear high-valent oxo-complexes are rather uncommon, likely because of their tendency to dimerize.[2] Manganese(V)-oxo species and their role in C-H oxidation reactions have been also explored,[3] also it have been studied in other oxidative transformations such as sulfide oxidations and epoxidations.

In this work, we have studied the reaction of C-H oxidation of dihydroanthracene as model substrate mediated by [^{R}PyTacn-Mn^{IV}(OH)$_2$] and [^{R}PyTacn-Mn^{IV}(OH)(O)] species containing different electronic groups on the pyridine ligand.[4] A comparative analysis of the kinetic parameters of these reactions, as well as the thermodynamic driving forces for such reactions have been performed.

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Keywords: *C-H activation; Kinetics; Manganese;*

P-0182

LUMINESCENCE PROPERTIES OF NOVEL METAL-ORGANIC FRAMEWORKS (MOFS) BASED ON LEAD(II) AND A FUNCTIONALISED BIPHENYL LINKER

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The structural features of MOFs are highly influenced by many factors, such as the coordination chemistry of the included metal ions, the nature of the organic building blocks, the synthetic templates, solvents, counter-anions, stoichiometry and pH value of the solution.[1]

Lead(II) complexes exhibit a wide variety of coordination numbers[2] and irregular geometries, as well as luminescence properties[3]. Here, we will present the synthesis of a novel MOF from lead(II) nitrate and the functionalised biphenyl linker 4,4'-dicarboxy-2,2'-dimethoxy-1,1'-biphenyl (**LH_2**) in the solvent mixture EtOH/H_2O (2/10) which led to the formation of a three-dimensional network with a Pb_6O_2 cluster as secondary building unit. Interestingly, luminescence investigations of the Pb-based MOF show only ligand (not lead) emission and excitation, which is influenced by included organic molecules, such as DMF. Thus, $[\{(Pb_6O_2)L_4\}]_n$ can be used as sensor for organic solvents.

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P-0183

COATING PT NANOPARTICLES WITH METHYLS: THE REACTION BETWEEN METHYL RADICALS AND PT-NANOPARTICLES SUSPENDED IN AQUEOUS SOLUTIONS

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Transition metal nanoparticles (NPs) are known as catalysts of various redox processes. Radicals are often intermediates in these processes. Recent studies[1, 2] point out that methyl radicals react in fast reactions, with rate constants $k > 1\times10^8\ M^{-1}s^{-1}$, with Au^o, Ag^o and TiO_2 NPs dispersed in aqueous solutions to form intermediates, (NP)-$(CH_3)_n$, in which the methyls are covalently bound to the NPs via σ bonds. These intermediates decompose to form ethane. Thus formally the particles efficiently "catalyze" the dimerization of the methyl radicals. The reported minimal lifetime of the (NP)-CH_3 transients (t) is surprisingly long, *e.g.* $t \geq 8$ and $t \geq 188$ sec for Ag^o and Au^o NPs, respectively[2].

Platinum is a known catalyst of a variety of processes and a common electrode. In many cases surface alkyl groups have been proposed as intermediates in these processes. It seemed therefore of interest to study the kinetics and mechanism of reaction of methyl radicals with Pt^o-NPs suspended in aqueous solutions. The results point out that methyl radicals react with Pt^o-NPs suspended in aqueous solutions in fast reactions. This reaction results in four different products The major product is stable methyl coated Pt^o-NPs, $(Pt^o$-NPs)-$(CH_3)n$. C_2H_6, C_2H_4 and some polymerization products are also formed. These observations are in accord with the polycrystalline nature of the Pt^o-NPs. Thus atoms at edges, corners and planes have different chemical properties. These results are clearly relevant to the understanding of catalytic and electrochemical processes occurring on Pt^o surfaces.

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Keywords: *radicals; stable intermediates; rate constants; transition metal nanoparticles; mechanisms of reaction;*

P-0184

CIRCULAR HELICATES AND A MOLECULAR PENTAFOIL KNOT

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Knots are being discovered with increasing frequency in both biological and synthetic macromolecules and have been fundamental topological targets for chemical synthesis for the past two decades. Here we present the synthesis of the most complex non-DNA molecular knot prepared to date:[1, 2] the self-assembly of five bis-aldehyde and five bis-amine building blocks about five metal cations and one chloride anion to form a 160-atom-loop molecular pentafoil knot (five crossing points). The structure and topology of the knot is established by NMR spectroscopy, mass spectrometry and X-ray crystallography, revealing a symmetrical closed-loop double helicate with the chloride anion held at the centre of the pentafoil knot by ten CH...Cl– hydrogen bonds. The one-pot self-assembly reaction features an exceptional number of different design elements.

The synthesis of eleven pentameric related cyclic helicates is also reported. The factors influencing the assembly process (reactant stoichiometry, concentration, solvent, nature and amount of anion) were studied in detail: the role of chloride in the assembly process appears not to be limited to that of a simple template and larger circular helicates observed with related tris(bipyridine) ligands with different iron salts are not produced with the imine ligands. Using certain chiral amines, pentameric cyclic helices of single handedness could be isolated and the stereochemistry of the helix determined by circular dichroism.

We anticipate that the strategies and tactics used here can be applied to the rational synthesis of other higher-order interlocked molecular architectures.

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Keywords: *Supramolecular chemistry; Circular dichroism; Bridging ligands; Self-assembly; Anions;*

P-0185

LOW TEMPERATURE SYNTHESIS OF GEL-NANOSTRUCTURED SILVER VANADIUM OXIDES CATHODE MATERIALS

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Silver vanadium oxides (SVO) have potential applications in rechargeable high-energy density lithium batteries and photo-catalysis due to their excellent electrochemical and photophysical properties. Recently, several researching groups have obtained different nanostructured SVO via hydrothermal treatments.

The main aim of this work is to determine the effect of initial synthesis conditions on the particle size and morphology of α-$AgVO_3$ and β-$AgVO_3$ SVO. The solution and hydrothermal $AgNO_3$/$NaVO_3$/H_2O systems were studied, considering the economic cost versus the health hazards and environmental risks of the initial reagents with respect to V_2O_5, NH_4VO_3 or Ag_2O. The particle size and morphology were checked by particle size analyzer, X-ray diffraction and electron microscopy.

With regard to the α-$AgVO_3$ and β-$AgVO_3$ compounds obtained at room temperature, the α-$AgVO_3$ compound transformation to β-$AgVO_3$ depends on the stirring time. The electron microscopy images indicate that in a first step tabular micro-sized crystals agglomerated in spherical particles crystallize, and in the second step nano-tubular morphologies of 300-400nm x10nm x 10nm grow. If ethanol is used as co-dissolvent, the tabular like single crystals are completely recovered by 300-30x200-20x10 nm nano-tabular crystals. The α-$AgVO_3$ to β-$AgVO_3$ transformation does not seem to affect the particle morphology. For the hydrothermal treatments at 120 and 180ºC, the β-$AgVO_3$ obtained at neutral pH conditions crystallize as orange powders; however those ones synthesized at slightly acidic pHs, and with a starting vanadium rich stoichiometry crystallize as orange-red gels. The electron microscopy images indicate that nano-tubular (100-200x0.5x0.5 nm) samples of β-$AgVO_3$ are obtained after one hour of hydrothermal treatment at 120ºC.

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Keywords: *Silver Vanadium Oxide; Hydrothermal synthesis; Nanotubes; Li-Ion Batteries;*

P-0186

COPPER COMPLEXES OF DIHYDROXYBENZALDEHYDE THIOSEMICARBAZONES: SYNTHESIS, CRYSTAL STRUCTURE AND BIOLOGICAL ACTIVITIES

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Four thiosemicarbazones ligands, $H_3T(1)$, $H_3M(2)$, $H_3E(3)$ and $H_3P(4)$ have been prepared with good yield by refluxing 2,4-dihydroxybenzaldehyde with N(4)-substituted thiosemicarbazide in ethanol ($H_3T(1)$ = 2,4-dihydroxybenzaldehyde thiosemicarbazone; $H_3M(2)$ = 2,4-dihydroxybenzaldehyde 4-methylthiosemicarbazone; $H_3E(3)$ = 2,4-dihydroxybenzaldehyde 4-ethylthiosemicarbazone and $H_3P(4)$ = 2,4-dihydroxybenzaldehyde 4-phenylthiosemicarbazone). Reactions of these ligands with copper acetates in the presence of 2,2'-bipyridine lead to the formation of copper(II) complexes of formulation [Cu(bpy)L](5-8) (bpy = 2,2'-bipyridine; L = doubly deprotonated thiosemicarbazones = HT(5); HM(6); HE(7) and HP(8)). These compounds were characterized and their nucleolytic, cytotoxicity and Topoisomerase I inhibition activities studied. X-ray diffraction study indicates that complex **5** is mononuclear and five coordinated with the doubly deprotonated thiosemicarbazone acting as a tridentate ligand coordinating through the phenolic oxygen, azomethine nitrogen and thiolate sulfur while 2,2-bipyridine as the *N,N'*-bidentate ligand. The trigonality index τ of 0.03 for **5** indicates that the coordination geometry around copper is close to a perfect square pyramidal. Nucleolytic and topoisomerase I inhibition activities seem to be dependent on the N(4) substituent of the thiosemicarbazone moiety.

Keywords: *DNA; cytotoxicity; schiff bases; enzymes; copper;*

P-0187

USING CRYSTALLIZATION DRIVEN SELF-ASSEMBLY FOR CONTROLLED ACCESS TO 2-D OVAL SHAPED ARCHITECTURES

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Crystallization driven self-assembly (CDSA) has previously been used to direct the controlled solution phase self-assembly of block co-polymers and reported morphologies have often focused on cylindrical structures.[1, 2, 3]

Here we report on recent investigations using CDSA to access 2-D architectures involving block copolymers consisting of a core of polyferrocenosilane (PFS) and coronae of polydimethylsiloxane (PDMS), polymethylvinylsiloxane (PMVS) and polyisoprene (PI). By judiciously choosing experimental conditions we have shown it possible to obtain access to regular, mono-dispersed oval shaped platelet structures. We have, in addition, obtained remarkable control over their size and growth and visualization of the epitaxial growth processes.

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Keywords: *block co-polymers; self-assembly; polyferrocenosilane;*

P-0188

COPPER(I)-DIOXYGEN ACTIVATION AT A NOVEL UNSYMMETRIC DINUCLEATING LIGAND

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Dioxygen plays important roles in many biological processes: it is the terminal electron acceptor in cellular respiration and it is used as oxidant in metabolic oxidation reactions catalyzed by metalloenzymes. Due to its inherent electronic structure, dioxygen is kinetically inert and it reacts slowly with organic molecules. In biological systems this kinetic barrier is overcome by reaction with redox active transition metals. For example, several dinuclear copper proteins are involved in dioxygen activation processes.[1] In this line, extensive work has been done on exploring the Cu/O_2 reactivity in homometallic symmetric synthetic model compounds which bind and activate O_2, forming reactive intermediates like superoxides, peroxides or metal oxide species.

Usually, O_2-activating enzymes present an unsymmetric active site in which the two metal centers are not equivalent. This lack of symmetry arises either from a distinct coordination environment in both sites (as in tyrosinase) or from the presence of two different metals (as in cytochrome c oxidase). Studies of O_2 activation at unsymmetric dinuclear sites are very scarce due the difficulty in preparing an adequate ligand scaffold capable of holding metal ions in different coordination environments.[2]

In this work we have studied the binding and activation of dioxygen at copper(I) centers using a novel nitrogen-based unsymmetric ligand with two different binding sites. The coordination site "chosen" by the copper center to perform oxygen activation depends on the nature of the other metal present.

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Keywords: *O-O activation; copper;*

P-0189

TIN OXIDE NANOPARTICLES VIA TWIN POLYMERIZATION FROM NOVEL TIN(IV) ALKOXIDES

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The development of synthetic strategies for nanostructured hybrid materials is currently a very active research area.[1] Twin Polymerization is a novel synthetic approach for nanostructured organic-inorganic hybrid materials and metal oxide nanoparticles. The special character of this concept is the formation of an organic and an inorganic framework on the same timescale starting from one monomer only. Interpenetrating networks are generated and produce the nanostructure of the material. We are interested in tin-containing hybrid materials, which have attracted e.g. for gas sensors,[3] solar cells,[4] and lithium ion batteries.[5] Here we present novel well-defined tin precursors for Twin Polymerisation such as $Sn(OCH_2C_4H_3O)_4$, $[Sn(OCH_2C_4H_3S)_4 \cdot HOCH_2C_4H_3S]_2$, $[Sn(OCH_2\text{-}2\text{-}OCH_3C_6H_4)_4?HOCH_2\text{-}2\text{-}OCH_3C_6H_4]_2$ and $[Sn(OCH_2\text{-}2,4\text{-}OCH_3C_6H_3)_4?HOCH_2\text{-}2,4\text{-}OCH_3C_6H_3]_2$. By the use of such tin precursors in polymerization reactions in melt and in solution we were able to prepare cross-linked nanocomposites from the type polymer/SnO_2. These materials are characterized by ^{13}C and ^{119}Sn NMR in the solid state and in solution, IR, elemental analysis, BET, TEM and oxidized to give tin oxid nanoparticles.

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Keywords: *Organic-inorganic hybrid composites; Tin; Nanoparticles; Polymerization;*

P-0190

SYNTHESIS AND STRUCTURAL STUDIES OF VANADIUM(V) SCHIFF BASE COMPLEXES DERIVED FROM SALICYLALDEHYDE AND BRANCHED-CHAIN AMINO ACIDS

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Asymmetric metal catalysis is in the focus of current chemical research, and in recent years several major breakthroughs have been achieved. It was one of the 2001 Nobel Prize laureates, Sharpless and coworkers, who reported on a highly promising asymmetric vanadium catalyst based on [VO(*acac*)$_2$] as early as 1977. Since then, the catalysis by vanadium compounds has been studied in detail. It was found that vanadium complexes with tridentate Schiff bases ligands are very effective catalysts of asymmetric oxidation of organic sulfides to sulfoxides, diastereoselective epoxidation as well as hydroxylation, bromination and oxidation of secondary alcohols to corresponding ketones. This contribution deals with the preparation and structural characterization of three new chiral dioxidocomplexes of vanadium(V) with Schiff bases: [$N(CH_2CH_2CH_2CH_3)_4$][VO_2(N-salicyliden-L-valinato)] (1), [$N(CH_2CH_2CH_2CH_3)_4$][VO_2(N-salicyliden-L-leucinato)] (2) and [$N(CH_2CH_2CH_2CH_3)_4$][VO_2(N-salicyliden-L-isoleucinato)] (3). Compounds 1, 2 and 3 crystallize in the enantiomorph space group $P2_12_12_1$ and are isostructural. The central atom of vanadium adopts distorted square pyramidal coordination and bonds to two oxido ligands and one Schiff base ligand, which provides 'ONO' set of donor atoms. Using ^{51}V NMR spectroscopy the behavior of the complexes in different solvents important in terms of future study of their catalytic properties has been studied. It was found that the prepared complexes do not decompose in acetonitrile even after 48 hours, while in aqueous solution hydrolysis takes place and vanadates are formed. The change in color of dichloromethane and chloroform solution from yellow to blue indicates that V(V) is reduced to V(IV) after several hours. Thanks to an extraordinary stability of the complexes in acetonitrile solution the specific optical rotation and CD spectra were measured, confirming that the prepared compounds are homochiral. The CD spectra were collected in solid state too, showing fine resolution of the electron transitions.

Keywords: *Vanadium; Chirality; Schiff bases;*

P-0191

SYNTHESIS AND CHARACTERIZATION OF A3B TYPE WATER-SOLUBLE UNSYMMETRICAL PHTHALOCYANINE

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Phthalocyanines have attracted considerable attention and present an important and active frontier, due to their interesting and useful biological, electronic, optical, catalytic, and structural properties. For this reason they exhibite a wide range of application in material science, catalysts, and medicine[1]. For example boron containing phthalocyanines are particularly promising for dual application in BNCT and PDT because of their strong absorptions in the near-IR where light penetration through tissue is substantially increased compared with visible light[2]. For a number of uses, phthalocyanines with two or more different substituents on the exterior of the ring system would be advantageous as in the case of water-soluble unsymmetrically substituted phthalocyanines. The most commonly used synthetic approach is the statistical condensation of two different phthalonitriles, diiminoisoindols, or related derivatives[3].

In this work, water-soluble A_3B type novel unsymmetrically substituted metallophthalocyanines have been synthesized by statistical condensation of a mixture of 4-dimethylaminoethylthio-phthalonitrile (A) and 2-hydroxyethylthio-phthalonitrile (B). All synthesized novel phthalocyanine compounds have been characterized by using their elemental analyses, FT-IR, UV-Vis, ^{1}H NMR, ^{13}C NMR and mass spectroscopic methods.

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Keywords: *Phthalocyanines; Asymmetric synthesis; Macrocycles;*

P-0192

PREPARATION OF METAL-FREE AND METALLOPHTHALOCYANINES BEARING BULKY ANTRACENE GROUPS VIA ESTERIFICATION

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Phthalocyanines are close relatives of the porphyrin macrocycles and are the parent compound of one of the most studied class of functional organic materials. Phthalocyanine and its derivatives displaying interesting photophysical properties, electron transfer ability and reduction–oxidation behaviour are studied for applications in electrophotography, photovoltaic cells, fuel cells and electrochromic displays[1].

The main restricting factor of phthalocyanines is a rather low solubility in organic solvents. Periferal substitution of phthalocyanines with alkyl, alkoxy, alkythio chains or bulky groups enhances their solubility drastically[2]. The introduction of carboxy or amino groups gives water-soluble products. Compared to unsubstituted parent metal phthalocyanines, ester-containing porphyrazines and phthalocyanines are highly soluble in chlorinated hydrocarbons[3].The synthesis of soluble phthalocyanines should provide them new optical, electronic, redox and magnetic properties which could increase the field of possible applications.

In this present study, metal-free and metallophthalocyanines (Co, Zn) bearing peripheral thioglycolic acid groups were synthesized by cyclotetramerisation of the corresponding phthalonitrile derivative[4]. All of these thioglycolic acid substituents of the metal-free and metallophthalocyanines were esterified with antracene-9-methanol for gaining better soluble and combining two photoactive moieties in the same molecule. The novel phthalocyanine compounds were characterized by elemental analyses, ^{1}H-NMR, FT-IR, UV-Vis and Mass spectroscopic techniques.

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P-0193

PHOTOSENSITIZED RUTHENIUMNITROSYL COMPLEXES FOR CONTROLLED NO-RELEASE

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Novel strategies in curing cancer diseases involvethe use of nitric oxide (NO) as a therapeutic agent.[1] Controlled release of NOvia light irradiation of photosensitive compounds gained a lot of interest inthe last years.[2] A number of rutheniumnitrosyl complexes are promising NO donors as metallo-pharmaceuticals.[3-4] The specific design ofthe NO-releasing properties of such compounds can be reached by the synthesisof tailor-made organic ligands. Novel biscarboxamide rutheniumnitrosylcomplexes [LRu(NO)Cl] based on the tetradentate ligands *N,N′*-bis(1--methylimidazole-2-carboxamide)-1,2-phenazine (L = mipab)and *N,N′*-bis(1-vinylimidazole-2-carboxamide)-1,2-phenazine(L = vipab) have been synthesized and were characterized via NMR, MS, IR andUV/VIS. The synthesis was realized via novel lithiated biscarboxamide ligands ofstrong basicity. The UV/VIS-spectra of the obtained complexes compared to a rutheniumNO complex based on *N,N′*-bis(1-methylimidazole-2-carboxamide)--1,2-benzene(L = bib) showed an impressive red shift of the lowest energy absorption bandfrom 350 nm to 470 nm, which equals the region of blue light. Duringirradiation with wavelengths in the range of 450 nm to 490 nm,the NO-release was measured by using a fluorescence assay (Anslyn's NO assay).

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Keywords: *Antitumor agents; Nitrogen oxides; Ligand design; Lithium;*

P-0194

GUTMANN DONOR AND ACCEPTOR NUMBERS FOR IONIC LIQUIDS

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In recent years, ionic liquids have been discussed as an outstanding class of solvents, due to their wide range of properties. Unfortunately, a detailed understanding of the interactions between ionic liquids and dissolved substrates and the resulting effects on chemical reactions is, in many cases, still missing. These interactions and their strength is influenced by many different factors, such as the strength of intermolecular van der Waals forces, the ability of a solvent to form hydrogen bonds, the polarity of the solvent, and especially important for ILs, the strength of intermolecular coulomb interactions. The quantification of these solvent characteristics can be an important tool to understand physicochemical phenomena and chemical behavior in solution.

One approach to express and quantify solvent properties is the so called “donor-acceptor concept” invented by Victor Gutmann. He defined the donor number, DN (also referred to as “donicity”), as a quantitative measure for the propensity to donate electron pairs to acceptors, and its counterpart, the acceptor number (AN), as a measure for the electrophilic properties of a solvent, i.e. the ability to accept electron pairs or at least electron density.

For the first time, we present Gutmann donor and acceptor numbers for a series of 36 different ionic liquids that include 26 different anions. The donor numbers were obtained by ^{23}Na-NMR and show a strong dependence on the anionic component of the ionic liquid. The donor numbers measured vary from -12.3 kcal mol^{-1} for the ionic liquid containing the weakest coordinative anion [emim][FAP] (1-ethyl-3-methylimidazolium tris(penta-fluoroethyl)-trifluorophosphate), being a weaker donor than 1,2-dichloroethane, to 76.7 kcal mol^{-1} found for the ionic liquid [emim][Br], exhibiting a coordinative strength in the range of tertiary amines. The acceptor numbers were measured using ^{31}P-NMR and also vary as a function of the anionic and cationic component of the ionic liquid.

Keywords: *ionic liquids; solvent properties; NMR-measurements; nucleophilicity;*

P-0195

A NOVEL IMMOBILIZED NI COMPLEX ON A SILICA-SUPPORT. A SPECTROSCOPICAL AND AN ELECTROCHEMICAL STUDY

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The reaction of silica gel particles with aminopropyl orthosilicate under a dry atmosphere gives a precursor with the amine group that can be readily used as a ‘padlocking’ nucleophile for ring closure. This study reports the first covalent binding of a nickel-penta-aza-cyclotetradecane complex through a non-coordinative nitrogen atom to silica gel particles. These grafted particles can serve as a good candidate for electron exchange columns (analogous to ion exchange columns). Redox cycles with persulfate as the oxidizing agent, and ascorbic acid as the reducing agent were performed. Modified electrodes based on Nafion with embedded “particles” (containing the NiL complex) have been prepared, and CV measurements have been conducted. The electrochemical measurements showed no changes in the redox potential ($E_{1/2}$ $Ni^{3+/2+}L'$= +0.750 volt vs. SCE) versus the redox potential of the analogous couple $Ni^{3+/2+}L$. The ESR measurements confirm the new Ni^{3+} formation. The redox behavior and full characterization of NiL' will be presented in detail.

Keywords: *nickel complexes; electron exchange columns; redox cycles; grafted particles; electrochemistry;*

P-0196

TIN-ENCAPSULATED ORDERED MESOPOROUS CARBON SPHERES FOR LI-ION BATTERIES

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Tin-based materials have been considered as a good candidate for anodes of Li-ion battery (LIB) because of their high capacity (Sn, 994 mAh g^{-1} and SnO_2, 781 mAh g^{-1}), abundance in earth, nontoxic, and chemical stable. However, the large volume changes during charge/discharge (Li is intercalated/deintercalated) processes cause the internal damage to the electrode, and the loss of capacity. In this study, the improvement in stability with high capacity retention has been demonstrated by embedding Sn particles into ordered mesoporous carbon spheres (TOMCS) which was synthesized for buffering the volume expansion during the insertion and removal of Li ions. A series of TOMCS with various weight percentages of tin ranging from 15 to 75 wt% has been obtained via the hydrothermal and impregnation method. The mesoporous structures of TOMCS in terms of morphology, crystallization, and surface area were characterized by scanning/transmission electron microscope (SEM/TEM), small angle/wide angle X-ray diffraction (XRD), and N_2 adsorption/desorption analysis, respectively. TOMCS exhibited the body-centered cubic mesoporous arrangement after calcination at 700 °C in N_2 and showed obvious Sn(0) and SnO_2 phases with the high surface area of around 700 m^2 g^{-1}. The electrochemical performances were displayed by Li half cell. An extremely high coulomb efficiency of 99% with the stable specific capacity of around 300 mAh g^{-1} after 100 cycles was obtained, which indicates that TOMCS can successfully accommodate large strain after lithiated electrochemical process. Results obtained clearly demonstrate that TOMCS is a novel material for anode fabrication for potential application to high rate capability and good cyclability LIB.

Keywords: *Li ion battery; Ordered mesoporous carbon spheres; Hydrothermal; Impregnation; Cyclability;*

P-0197

SOLID STATE STRUCTURE OF A NEW NHC-BASED CYCLOMETALATED PLATINUM(II) COMPLEX

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Phosphorescent platinum(II) complexes have attracted much attention as promising emitters for application in organic light-emitting diodes (OLEDs) because their exceptional luminescence properties. We recently reported a new class of platinum(II) compounds with cyclometalated N-heterocyclic carbene (NHC) ligands based on phenylimidazole. The complexes are strongly emissive in the green-blue region of the spectrum and their properties differ from the previously known complexes with C^N cyclometalating ligands derived from e.g. 2-phenylpyridine (ppy) or from phenylazoles like phenylpyrazole or 2-phenylimidazole.

In this presentation we show and discuss the second solid state structure of this new class. The platinum(II) complex contains a bidentate, cyclometalated phenylimidazol-ylidene ligand and an acetylacetonate spectator ligand, which form a distorted square planar coordination sphere around the platinum center. In the crystal the molecules are oriented in a parallel fashion caused by their planarity and several intermolecular interactions.

Keywords: *Carbene ligands; Platinum; Solid-state structures;*

P-0198

SYNTHESIS AND REDUCTION OF A HYPER-COORDINATED CATION [L-PCL$_2$-AL]+ (L = NHC, AL = ABNORMAL NHC)

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Positively charged, hyper-coordinated organophosphorus compounds are an interesting and rather undeveloped substance class.[1] They can be used as models for the mechanism of nucleophilic substitution reactions at a phosphorus-center. Therefore, we investigated the reaction of **[LPCl$_2$][OTf]**[2] (L = 1.3-bis(2.6-diisopropylphenyl)imidazol-2-ylidene) and L in difluorobenzene. The outcome of this reaction is cation [**L-PCl$_2$-*a*L**]$^+$ in which the phosphorus atom is *pseudo*-penta-coordinated by two Cl-substituents, a normal (**L**) and abnormal (*a***L**) NHC. Reaction of [**L-PCl$_2$-*a*L**]$^+$ with KC_8 or Mg leads to the clean formation of the P(I)-centered cation [**L-P-*a*L**]$^+$. The intriguing reaction and bonding situation of cations [**L-PCl$_2$-*a*L**]$^+$ and [**L-P-*a*L**]$^+$ will be discussed.

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Keywords: *Maingroup; Phosphorus; Cation; Hyper-coordinated; Reduction;*

P-0199

PALLADIUM(II) COMPLEXES WITH CHELATING BISCARBENE LIGANDS IN THE SUZUKI-MIYAURA CROSS COUPLING REACTION

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Palladium catalyzed cross coupling reactions are one of the most powerful carbon-carbon bond-forming processes. The Suzuki-Miyaura cross coupling reaction has become a very important and widely used method in fine chemical syntheses. Since the isolation of a stable free *N*-heterocyclic carbene (NHC) in 1991 a large number of palladium-NHC complexes have been investigated.

We studied the catalytic activity of palladium(II) complexes with chelating imidazolium and benzimidazolium ligands in the Suzuki-Miyaura cross coupling reaction. *N*-aryl substituted bis-NHC-Pd complexes could be synthesized in three steps starting from commercially available anilines. The methylene bridged systems with aryl substituents carrying sterically and electronically different groups (F, NO_2, OMe, H, Me, *i*-Pr) show good to excellent catalytic activities in the Suzuki-Miyaura cross coupling reaction of aryl bromides. We have shown that ligands substituted with electron donating groups lead to higher yields, sterically demanding ligands to lower yields in the Suzuki-Miyaura cross coupling of aryl bromides. The *p*-methoxy phenyl-substituted bis-NHC-Pd complex turned out to be the most active complex.

Furthermore the *p*-methoxy phenyl-substituted bis-NHC-Pd complex shows a good substrate scope. Aryl bromides with electron withdrawing as well as donating groups in *para* position and *ortho* and di-*ortho* substituted aryl bromides were coupled in excellent yields.

Keywords: *Cross-coupling; Palladium; Carbene ligands;*

P-0200

FUNCTIONALIZATION OF KREBS-TYPE POLYOXOTUNGSTATES WITH 4-IMIDAZOLECARBOXYLATE

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Functionalization of polyoxometalates (POMs) via covalent attachment of organic ligands represents a suitable strategy to obtain hybrid derivatives of this class of anionic clusters with new properties and applications [1]. Several routes have been explored to prepare such hybrids, including ligand substitution of labile water molecules on 3d-substituted POMs. Despite of being ideal candidates because of their two external 3d atoms with three water molecules each, Krebs-type $[M_2(H_2O)_6(WO_2)_2(XW_9O_{33})_2]^{n-}$ polyoxotungstates [2] remain almost unexplored as POM precursors in ligand substitution and only oxalate derivatives of iron(III) tetra-substituted clusters are known[3].

Here we report the direct functionalization of 3d-disubstituted Krebs-type POMs with 4-imidazolecarboxylate (L), which has resulted in two complete families of organically derivatized $[\{M^{II}(L)(H_2O)\}_2(WO_2)_2(XW_9O_{33})_2]^{12-}$ tungstoantimonate(III) and –bismuthate(III) species, where M = Mn, Co, Ni, Zn. The title POMs have been prepared by straightforward ligand substitution on pre-formed precursors, but also by addition of L to solutions of Krebs-type POMs generated in situ or even to solutions of addenda-metal and heteroatom sources.

Functionalization has been spectroscopically determined prior to single-crystal X-ray studies. The title species are formed from two $[B\text{-}\beta\text{-}X^{III}W_9O_{33}]^{9-}$ subunits linked by two octahedral $\{WO_2\}$ internal moieties and two external M^{II} atoms, resulting in the well-known Krebs-type skeleton. Each M^{II} center is octahedrally coordinated by three O_{POM} atoms, one O,N-chelating ligand and one water molecule. The hybrid POMs show a one-dimensional arrangement in the solid state through triple hydrogen-bonding between the imidazolyl N-H groups and bridging O atoms of tetrameric $\{W_4O_{18}\}$ faces.

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Keywords: *Polyoxometalates; Hybrids; Functionalization;*

P-0201

SYNTHESIS AND CHARACTERIZATION OF COORDINATION CAGES VERSUS SPHERICAL MORPHOLOGY USING PYRIDYL-CONTAINING TRIDENTATE LIGANDS

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In order to validate the formation and behavior of cage containing a flexible tridentate ligand, we report cage compounds, $[Pd_3(\mathbf{L1})_2](X)_6$ (Pd = $(Me_4en)Pd(II)$; X^- = BF_4^- and ClO_4^-; **L1** = 1,3,5-tris(isonicotinoyloxyethyl)cyanurate) via construction of a new C_3-symmetric potential triangular component with *cis*-protected ditopic $(Me_4en)Pd(II)$ as a corner linker. A single water molecule is nestled within the new cage, and is reversibly adsorbed and desorbed via a combination of the adequate space, polar environment, and conformational flexibility of the cage. Thus, the duality of liberal and restrictive properties of a single water molecule has been discussed based on spectroscopic data. In Suzuki-Miyaura C-C cross-coupling reactions, the cage complex shows significant catalytic activity along with the effects of the isolated single water molecule. On the other hand, reaction of $(bpy)Pd(PF_6)_2$ (bpy = 2,2'-bipyridine) with 1,3,5-tris(nicotinoyloxyethyl)cyanurate (**L2**) in acetone, and followed by addition of water and solvent evaporation allows to form amorphous spherical morphology consisting of $[(bpy)_3Pd_3(\mathbf{L2})_2](PF_6)_6$ without any template or additive. In contrast, the reaction and slowly evaporation in acetone for 1 month yield single crystals consisting of $[(bpy)_3Pd_3(\mathbf{L2})(\mu_3\text{-}HPO_4)](PF_3(OH)_3)$. The formations of spherical morphology and cage-shaped single crystal appear to be primarily associated with the kinetic and thermodynamic control, respectively. The present compounds were characterized by IR, ^{31}P NMR, and thermal analyses.

Keywords: *Cage compounds; Tridentate ligands;*

P-0202

DITOPIC MO(VI) DIAMINOTETRAPHENOLATE COMPLEXES

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Oxidomolybdenum(VI) compounds act as effective catalyst for olefin metathesis reactions[1], oxidation of alcohols[2], epoxidation[2], and oxotransfer[4] reactions.

Cis-dioxidomolybdenum(VI) complexes with aminobisphenols are easily prepared using various molybdenum starting materials in polar solvents. The coordination sphere around Mo(VI) cation in these complexes is predominantly octahedral, and Mo(VI) bonds tightly to hard Lewis bases. In order to increase the reactivity and catalytic activity of the complexes, some labile ligands, e.g. halides are needed on the coordination sphere of Mo(VI).[5] Earlier we have modified aminobisphenol complexes of dioxidotungsten(VI) and -molybdenum(VI) by the reaction with trimethylsilylchloride.[6] In most cases the reaction produces *cis* and *trans* isomers of the new $[MoOCl_2]^{2+}$ moiety whereas the *trans* isomer is more stable.[6]

In this work we report linear ditopic dioxidomolybdenum(VI) diaminotetraphenolates with *n*-alkyl-bridged *N,N,N',N'*-tetra(2-hydroxybenzyl)diamines. Similar ligands are earlier used to form cyclic dinuclear Cu(II) complexes.[7] Chloride-for-oxide substitution for the prepared compounds as well as some catalytic results are also presented.

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Keywords: *Mo(VI); aminobisphenol; catalysis;*

P-0203

NOVEL DIENE LIGANDS IN RHODIUM-CATALYZED 1,4-ADDITION

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The synthesis and catalytic activity of new diene ligands is an ongoing research topic of high interest.[1–2] Among the dienes bicyclic strained olefins with interesting electronic properties and reactivity are presented by benzobicyclo[2.2.2]-2,5,7-octatriene, a combination of an aromatic and a barrelene framework.[3] In the last decades several synthetic strategies for such benzobarrelenes have been developed.[4–7] Recently, the activity and enantioselectivity of rhodium-catalyzed 1,4-addition with chiral tetrafluorobenzobarrelene-based ligands was reported.[8]

Herein, we present a novel Diels-Alder type synthesis route for benzobarrelenes bearing substituents at the aromatic ring. Starting from the Grignard reagent (2,4,6-Tribromphenyl)-magnesiumbromide we obtained dibromoarynes, which were reacted with several benzene derivates to give dibromobenzobarrelenes. The synthetic concept gives access to diverse benzobarrelenes including carboxylic and phosphonic acid derivates. The high high catalytic activity of "in-situ" formed rhodium complexes for 1,4-addition with quantitative conversion is shown.

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Keywords: *diene; catalysis; benzobarrelene; 1,4-addition; ligand;*

P-0204

EXPERIMENTAL AND THEORETICAL STUDIES ON THE REACTIVITY OF SILICON CONTAINING PRECURSORS FOR TWIN POLYMERIZATION

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There has been an increasing interest in novel synthesis strategies for porous materials within the last decade. This is related to the numerous industrial applications which take advantage of the particular structural features of nanomaterials. Especially organic-inorganic hybrid materials with well defined nanoscaled pore geometry, high porosity and monodisperse particle size distribution have become an important field of research. Most of the synthetic concepts for such materials provide organic-inorganic composite materials, which exhibit nanostructures in the range between 2 to 100 nm.[1] The novel concept of *Twin Polymerization* provides a synthesis route towards nanoscaled metal oxides as well as metal oxide based organic-inorganic composite materials with domains in the range below 2 nm.[2] For instance, *Twin Polymerization* of 2,2'-Spirobi[4*H*-1,3,2-benzodioxasiline] gives a composite material composed of interpenetrating SiO_2/Phenol resin networks with defined nanostructured domains of 0.5 to 3 nm. Oxidation of the composite material leads to highly porous SiO_2 with a BET surface area of 904 $m^2 g^{-1}$, while carbonization and consecutive removal of SiO_2 gives microporous carbon with a BET surface area of 1018 $m^2 g^{-1}$.[2a] Here we present the synthesis and characterization of new *Twin Monomers* such as 6,6'-Dimethyl-4*H*,4'*H*-2,2'-spirobi[benzo-1,3,2-dioxasiline] and 6,6'-Dibromo-4*H*,4'*H*-2,2'-spirobi[benzo-1,3,2-dioxasiline]. Their reaction behavior with regard to *Twin Polymerization* was studied and the resulting organic-inorganic composite materials were characterized. In order to support our hypothesis of a reactivity scale based on steric and electronic features of the monomers, we have carried out DFT calculations (B3LYP//def2-TZVPP level of theory) in order to obtain more detailed insight into the first reaction steps of this novel type of polymerization.

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Keywords: *Twin Polymerization; DFT Calculations; nanoscaled Hybrid Materials;*

P-0205

NEW MO(II) HETEROGENEOUS MATERIAL FOR ENANTIOSELECTIVE CATALYSIS

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Chiral porous materials have many potencial applications in a wide range of areas, such as enantioseparation, chiral catalysis, chemical sensors, drug delivery, chiral catalysis.[1]. In this work, the synthesis of chiral matrix mesoporous materials was achieved using ammonia as co-surfactant[2]. They were used as support to prepare chiral molybdenum(II) heterogeneous catalysts to be tested in enantioselective oxidation catalysis. The materials prepared retain the basic structure of the silicon based matrices, but they also display a confined helical environment of the channels, as detected by SEM and TEM.

The inner surface of the chiral material was functionalized by reaction of surface SiOH groups with the ligand $C_5H_4NCH{=}N(CH_2)_2CH_3$ (pyca) or a chiral ligand (glypy, a 2-aminopyridine glycidyloxypropyl derivative). Both ligands were modified to bear adequate $Si(OR)_3$ groups, to allow covalent binding to the walls of the material. The immoblized ligands react with $MoI_2(CO)_3(NCMe)_2$ precursor complex, giving rise to heterogeneous catalysts[3, 4]. All synthesized materials were characterized by means of adequate spectroscopic techniques, such as solid state NMR, FTIR, XRD, SEM/TEM, and N_2 isotherms. The chiral materials were tested as precursors in oxidation catalysis, namely, epoxidation of olefins and allylic alcohols, with *t*-butylhydroperoxide. Several substrates were tested, from cyclooctene and styrene, to chiral species such as r-limonene, cis-hexen-3-ol, trans-2-hexen-1-ol and other allylic alcohols.

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Keywords: *Molybdenum; Mesoporous materials; Enantioselectivity; Epoxidation;*

P-0206

ACIDIC WET CHEMICAL ETCHING OF SILICON – FROM SURFACE CLEANING TO TEXTURING

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Acidic wet chemical etching processes are widely utilized in semiconductor and photovoltaic industry (cleaning silicon, texturing of multicrystalline silicon wafers and recycling of silicon). In spite of numerous industrial applications, detailed understanding of the etching process is still missing. However, dissolving silicon requires a stepwise oxidation of silicon surface atoms by oxidants (HNO_3, NO_2^+, NO^+, H_2O_2,…) and the formation of soluble complexes by fluoride containing species (HF, HF_2^-, F^-). Both processes proceed simultaneously at the silicon/etchant interface. Cleaning solar-grade silicon is realized by acidic and alkaline solutions. Because of environmental aspects, a substitution of HF-HNO_3-based mixtures by HF-H_2O_2-containing solutions is of increasing interest.[1] For etching silicon in HF-H_2O_2-H_2O mixtures concentration depending reactivity studies were performed. Especially metal contaminations influence the reactivity of silicon in HF-H_2O_2-H_2O solutions. Resulting surfaces were analyzed by means of scanning electron microscopy (SEM) and the formation of porous silicon was obtained. However, HF-H_2O_2-H_2O mixtures are suitable for cleaning of small sized silicon particles. During processing solar cells, HF-HNO_3-based etching mixtures are used for texturing silicon wafers. Thereby, sulphuric acid is a reasonable additive.[2, 3] HF-HNO_3-H_2SO_4 etching mixtures were characterized by means of NMR and Raman spectroscopy. For high sulfuric acid concentrations, a stabilization of nitrogen-oxygen cations (NO_2^+ and NO^+) was obtained. Depending on mixture compositions, silicon etching rates and etched surface morphologies were investigated. In general, the H_2SO_4-concentration influences the mixture reactivity and etched surface morphologies. Surprisingly, pore-like etching structures were obtained by SEM and laser scanning microscopy (LSM) for H_2SO_4-rich mixtures.[4]

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Keywords: *Silicon; Surface chemistry; Surface analysis; Sustainable Chemistry;*

P-0207

SYNTHESIS OF NEW TITANIUM OXO CLUSTERS USING PHOSPHONIC ACID DERIVATIVES

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Clusters are interesting intermediates between molecules and nanoparticles. Unlike nanoparticles they are formed as defined and soluble compounds, the structure of which can be determined exactly by single crystal XRD and NMR. A versatile route to metal oxo clusters are reactions of metal alkoxides with carboxylic acids. The metal alkoxides are partly hydrolysed by water produced *in situ,* through esterification of the acid. Controlled condensation is thus achieved, and well defined clusters are formed, which are stabilized by the carboxylate ligand sphere.

New oxo clusters were prepared by varying the carboxylic acids and using mixtures of different carboxylic acids. Furthermore, using phosphonate ligands for the clusters, new highly interesting compounds were synthesised. By employing easily hydrolysed phosphonic acids esters, namely trimethylsilyl esters, instead of phosphonic acids themselves, the reaction is convenient and the results are better reproducible.

A new cluster, the first titanium oxo cluster with functionalized phosphonate ligands, was thus formed. Its structure consists of six titanium atoms and two oxo bridges. Six phosphonates are bound to three titanium atoms each, opening two interconnected tetrahedrons. Interestingly, the cluster has an overall rod-like shape, with only alkoxides ligands on both tips.

Keywords: *Cluster compounds; Titanium;*

P-0208

SYNTHESIS OF CATIONS [LPCL$_2$]$^+$, [L$_2$PCL]$^{2+}$ AND [L$_3$P]$^{3+}$ AND SUBSEQUENT REACTIONS (L = NHC)

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Several types of phosphorus-centered cations are known, however, most of them require stabilization *via* adduct formation with a Lewis base.[1] Multiply-charged phosphorus-centered cations incorporating trivalent P(III)-atoms that are suitable for further functionalization are rare.[2]

In this contribution we present phosphorus-centered cations **[LPCl$_2$]$^+$**, **[L$_2$PCl]$^{2+}$** and **[L$_3$P]$^{3+}$** that are synthesized from the reaction of PCl$_3$ with "imidazolium-transfer" reagents[3] which are prepared from N-heterocyclic carbenes (NHC's) and Me$_3$SiOTf.[4]The cations are formed *via* sequestration of the chloro-substituent into Me$_3$SiCl. This approach can be extended to the arsenic derivative **[LAsCl$_2$]$^+$**. Substitution reactions have been investigated with Me$_3$SiCN, Me$_3$SiN$_3$, (Me$_3$Si)$_2$S and reduction reactions to access novel functionalized P(III) derivatives.

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Keywords: *Cations; Main Group Elements; Phosphorus; Sulfur Heterocycles;*

P-0209

CYCLOPENTASILANE (CPS) AS A PRECURSOR FOR POLYSILANES AND SILICON COATINGS

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Chemical Vapour Deposition (CVD) of monosilane is a well-known method for the synthesis of solar-grade silicon, e.g. for thin-film solar cells or thin-film transistors. The use of bulky vacuum apparatus and high energy consumption make the process expensive. An alternative approach is based on liquid perhydridooligosilanes as precursors combined with liquid deposition techniques such as spin- or spray-coating to yield thin silicon-films after a pyrolysis. Shimoda et al.[1, 2] reported on cyclopentasilane[3] (Si$_5$H$_{10}$/ CPS) as precursor for solution-processed silicon thin-films.

We report on an improved synthesis of CPS, replacement of the common hydrogenation agent LiAlH$_4$, which can lead to polymerization and aluminium impurities. The use of alkylstannanes leads to perhydridooligosilanes. Photo-polymerisation of CPS provides soluble oligomers. Pyrolysis of the perhydridooligosilanes generates cross-linked polymers as well as amorphous and crystalline silicon films. Thermogravimetry and DSC experiments coupled with mass spectroscopy provide information on the thermolysis process. Analysis of the oligomeric intermediates and the solid products was performed with FTIR, Raman and ^{29}Si NMR spectroscopy. Further information on the chemical structure and physical properties of the coatings is provided by ellipsometry, XPS, electron microscopy and conductivity measurements.

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Keywords: *Polymerization; Silicon; Amorphous materials;*

P-0210

SOLID-STATE ION EXCHANGE OF CU2+ AG+ AND LI+ ON HY ZEOLITE. ION EXCHANGE KINETIC STUDY

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The areas of technological applications of ion exchange associated to zeolite materials are progressively increasing and have attracted ever-growing attention during the past two decades. These include uses in catalysis, the removal of nuclear waste or other environmental pollutants, ion chromatography and detergency [1, 2]. Conventionally, ion exchange is commonly done by suspending the zeolite powder in aqueous solutions of salts, which contain the desired in-going cation. The major side effect of this ion exchange method, compared to solid-state ion exchange (SSIE) technique, is the hydrolysis effects that may alter the zeolite structure and the adsorption properties [1–3]. SSIE technique has not been as extensively studied because of the complexity of the process. Information related to the ion exchange reaction within zeolites and their dependence to the nature of in-going cation is limited and associated phenomena are not well understood. In the present study, Ag-, Cu- and Li-exchanged zeolites are prepared by the SSIE method. Reactive mixtures of HY zeolite and salts containing the in-going cation ($AgNO_3$, $CuCl_2$ or $LiNO_3$) are reacted at high temperature in pyrex fixed bed reactor. The ion exchange kinetic is followed using pH-metry measurement of the acidic gas leaving the reactor (HNO_3 or HCl) and reacting with alkaline solution. On other hand, the produced acid is estimated via thermogravimetry. Both structural and textural investigations show good conservation of the zeolitic structure after ionic exchange. The ion exchange kinetic study highlights clearly the complexity of the diffusive mechanisms of ions within the micropores of exchanged zeolites.

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Keywords: *Zeolites; Microporous materials; Ion exchange; Solid-state reactions;*

P-0211

SYNTHESIS OF SINGLE SOURCE PRECURSORS FOR NI/ZRO$_2$ NANOCOMPOSITES

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Many natural materials consist of inorganic and organic building blocks, i.e. they are inorganic-organic hybrid materials. The concept of hybrid materials is used to study fundamental processes of materials formation and to transfer ideas to artificial materials. One of the greatest advantages of hybrid materials is the possibility to create multifunctional materials.

In the work presented here, bimetallic nanocomposites are prepared by means of inorganic-organic hybrid intermediates. To this end, single-sourse precursors for sol-gel processing were prepared. Organic moieties containing two functional groups are used which

(**a**) connect two different metal moieties.

(**b**) are stable during sol-gel processing.

(**c**) allow some pre-orientation of the two metals.

In this presentation, a compound with both a Schiff base and a carboxylate group was employed as bridging ligand in the synthesis of heterobimetallic (Ni/Zr) complexes. The resulting complex was processed by the sol-gel method, followed by calcination to remove the organic linker. The non-hydrolytic sol-gel method is also promising. The complex was characterised by NMR and IR spectroscopy and the resulting mixed oxide by SAXS measurements.

Keywords: *Sol-gel processes; Zirconium; Nickel;*

P-0212

SYNTHESIS OF SILICOPHOSPHATES CONTAINING SIO6 OCTAHEDRA

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In nature, silicon predominantly appears in tetrahedral coordination. A few high-pressure phases are known such as stishovite [1, 2] where silicon is in an octahedral coordination. Meanwhile, it was also proved that six-fold coordinated silicon is present in a small number of silicophosphates. Examples with SiO_6 octahedra are SiP_2O_7-I [3], SiP_2O_7-III [4], SiP_2O_7-IV [5] and $Si_5P_6O_{25}$ [6]. However, for their synthesis high temperatures, transport reactions or the addition of alkali or alkaline earth halides are frequently required.

Here, we present a novel synthesis of silicophosphate solids with octahedral silicon structures at room temperature and under normal pressure [7]. Anhydrous H_3PO_4 and alkoxysilanes were used to form Si/P/O-materials comprise SiO_6 and SiO_4 units plus PO_4tetrahedra. The products were fully characterized with ^{29}Si-, ^{31}P-, ^{1}H-NMR-, IR-spectroscopy and single crystal X-ray structure analysis.

The new preparative route opens opportunities to prepare further silicophosphates and related materials.

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Keywords: *Silicon; Phosphorus; Coordination modes;*

P-0213

C^C*-CYCLOMETALLATED PLATINUM(II) COMPLEXES WITH TRIFLUOROMETHYL-ACAC LIGANDS – SYNTHESIS AND ELECTRONIC EFFECTS

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A series of C^C*-cyclometallated platinum(II) trifluouromethyl-acac complexes could be synthesized via a new synthetic route.

They have been characterized by standard methods (NMR, EA) as well as solid-state structures. Quantum chemical calculations on the HOMO and LUMO levels show significant differences to the previously reported acac-derivatives.

Keywords: *platinum; carbene ligands; Density functional calculations; Solid-state structures; Photophysics;*

P-0214

A SULFONYL SUBSTITUTED DILITHIO METHANDIIDE: FROM ITS ELECTRONIC STRUCTURE TO TRANSITION METAL CARBENE COMPLEXES

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Since the pioneering work by E. O. Fischer and R. R. Schrock, transition metal carbene complexes have found wide-ranging applications. These complexes are generally divided into two classes, the Fischer-type carbene and the Schrock-type alkylidene complexes. However in this context, carbene complexes formed from geminal dianions, above all dilithiated bis(iminophosphorano) and bis(thiophosphoryl)methanes, have gained special interest as they seem to contradict this general classification pattern.[1] Here, the metal carbon bond is formed by a four-electron donation from the ligand to the metal, resulting in a highly nucleophilic carbon atom.[2]

Investigations have so far concentrated on the readily available bis(phosphonium) systems, thus leaving the impact of the α-substituent on the nature of the metal carbon bond and thus on the reactivity of the complex unknown. However, electronic effects of substitutents at the carbene carbon have shown to crucially influence the electronic properties and reactivity of carbene complexes. Here we present a novel sulfonyl substituted dilithio methandiide as precursor for transition metal carbene complexes.[3] The methandiide features a distorted carbon environment which differs from the ideal tetrahedral arrangement. This is mainly due to geometrical restriction of the donor functions and can be described by two different bonding modes of the lithium atoms with the sp^2hybridized carbon atom. Transmetallation with metal salts gives way to early and late transition metal carbene complexes in high yields.

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Keywords: *lithium; carbene; carbanions; transition metals;*

P-0215

SWITCH IT! – PHOTOCHROMIC CARBENE LIGANDS

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N-Heterocyclic carbenes (NHC) are established ligands for almost all transition metals and various highly active catalyst systems bearing NHC ligands have been reported. Nevertheless, the control of their catalytic performance by external stimuli is still a challenging task. Various concepts for the regulation of the activity including the variation of the pH-value, temperature or solubility have been introduced, but besides the activation of precatalysts by irreversible photolytic reactions the reversible regulation of catalysts by light is still in its infancy [1]. Promising candidates for this purpose are photochromic systems which can be switched between two different states, e.g. diazobenzenes or spiropyranes. Based on these moieties, ligands can be designed which are capable of reversibly shielding an active center of a metal complex catalyst by steric hindrance.

We will present our first results of NHC based ligands bearing a diazobenzene group and demonstrate their ligand properties by the synthesis of the corresponding Ag(I) and Au(I) complexes. The Ag(I) complex is obtained by the reaction of the functionalized imidazolium salt with Ag_2O, successive transmetallation with $(Me_2S)AuCl$ yields the Au(I) complex. The *E->Z* isomerisation is induced by UV-light. The thermal back reaction is very slow and account for minutes even at 80 °C making an effective switching under catalytic conditions feasible.

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Keywords: *Photochromism; Carbene ligands; Gold; Silver;*

P-0216

PHOTOCHEMICAL, PHOTOPHYSICAL AND BIOLOGICAL PROPERTIES OF NOVEL WATER SOLUBLE PHTHALOCYANINES BEARING TRIFLUOROMETHYLQUINOLINE GROUPS

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For photodynamic therapy (PDT), a combination of a photosensitizing drug and light in the presence of molecular oxygen is used to obtain a therapeutic effect, and has been proposed as an alternative treatment to complement conventional protocols in the management of malignant tumours and many other nononcologic diseases [1]. The use of photosensitizing agents for inactivation of several cancer cells has been widely studied [2]. Due to their high molar absorption coefficient in the red part of the spectrum, photostability, and long lifetimes of the photoexicited triplet states, phthalocyanines (Pcs) are known to be useful photosensitizers [3, 4]. The aggregation properties of Pcs are very important for the development of new photosensitizers [5].

The aim of our ongoing research is to synthesize water-soluble phthalocyanines to be used as potential PDT agents. In this work; photophysical, (fluorescence quantum yields and lifetimes), photochemical (singlet oxygen and photodegradation quantum yields) and biological properties of water soluble quarternized metal free, zinc and indium phthalocyanines including trifluoromethylquinoline substituents on the peripheral positions are presented.

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Keywords: *DNA; Singlet oxygen; Phthalocyanines; Photodynamic theraphy;*

P-0217

REVERSIBLE PHASE TRANSFORMATION AND MECHANOCHROMIC LUMINESCENCE OF ZN(II)- AND CD(II)-DIPYRIDYLAMIDE COORDINATION FRAMEWORKS

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A 1-D double-zigzag framework, $\{[Zn(paps)_2(H_2O)_2](ClO_4)_2\}_n$ (**1**) (paps = N,N'-bis(pyridylcarbonyl)-4,4'-diaminodiphenyl thioether), was synthesized by the reaction of $Zn(ClO_4)_2$ with paps. However, a similar reaction, except that dry solvents were used instead, led to the formation of a novel 2-D polyrotaxane framework, $[Zn(paps)_2(ClO_4)_2]_n$ (**2**). The above difference relies on the fact that water coordinates to the Zn(II) ion in **1**, but ClO_4^- anion coordination is found in **2**. Notably, both structures can be interconverted by heating and grinding in the presence of moisture, and such structural transformation can also be proven experimentally by powder and single-crystal X-ray diffraction studies. The related papo (papo = N,N'-bis(pyridylcarbonyl)-4,4'-diaminodiphenyl ether) and papc (papc = N,N'-(methylenedi-*p*--phenylene)bispyridine-4-carboxamide) ligands were used to react with Zn(II) ions as well. When we performed a similar reaction with dry solvents, except that papo was used instead of paps, the product mixture contained mononuclear $[Zn(papo)(CH_3OH)_4](ClO_4)_2$ **(5)** and the polyrotaxane $[Zn(papo)_2(ClO_4)_2]_n$ (**4**). From the PXRD data, grinding this mixture in the presence of moisture resulted in the total conversion to the pure double-zigzag $\{[Zn(papo)_2(H_2O)_2](ClO_4)_2\}_n$ (**3**) immediately. Upon heating the double-zigzag **3,** the polyrotaxane framework of $[Zn(papo)_2(ClO_4)_2]_n$ (**4**) can be recovered. The double-zigzag $\{[Zn(papc)_2(H_2O)_2](ClO_4)_2\}_n$ (**6**) and polyrotaxane $[Zn(papc)_2(ClO_4)_2]_n$ (**7**) can be synthesized in a similar reaction. Although heating the double-zigzag **6** can undergo structural transformation to give the polyrotaxane **7**, grinding its solid samples in the presence of moisture cannot lead to the formation of the double-zigzag **6**. Significantly, the bright emissions for double-zigzag frameworks of **1** and **3** and weak ones for polyrotaxane frameworks of **2** and **4**, respectively, can also show interesting mechanochromic luminescence. The related Cd(II)-dipyridylamide coordination frameworks have been also investigated for the comparison purpose.

Keywords: *phase transformation; mechanochromic luminescence; coordination frameworks;*

P-0218

HIGHLY STRUCTURED AND HIGH SURFACE SS-SIC FROM PLANT MATERIAL

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The high-temperature-resistant silicon carbide, SiC, with interesting mechanical, chemical as well as electrical properties and the potential for widespread applications in electronics, semiconductor industry and catalysis is experiencing a new wave of interest. Purity, structural parameters and morphology play a key role influencing the performance of final application. Complex morphologies, high specific surface areas and high silicon content offer an important potential for high performance ceramics from plant materials.

Silicon carbide syntheses via carbothermal processes are known since years [1]. We are now able to produce highly structured biomorphous SiC with the possibility to transfer typical plant morphologies from renewable plant materials, especially for two*Equisetaceae* species, in a one step procedure at relatively low temperatures (approximately 1200 °C). A silicon-carbon-mixture, given by the plant itself [2], is used as precursor. The finely dispersed carbon precursor is prepared by pyrolysis of the organic plant matrix. Yields are between 3 to 100 % and we obtain high specific surfaces up to 660 m^2 g^{-1} depending on reaction parameters for the pure β-SiC [3]. The reported thermal synthetic method is, therefore of interest for applications where a pure, porous, thermally and chemically stable, as well as a cheap and easily available material is needed.

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Keywords: *Ceramics; Biomass; Carbides;*

P-0219

NMR INVESTIGATIONS OF THE INTRA- AND INTERMOLECULAR EXCHANGE PHENOMENA OF THE 3,5-DIMETHYLPYRAZOLYL SILANE CLSI(PZ*)$_3$ AND RELATED COMPOUNDS

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Chlorine substituted 3,5-dimethylpyrazolyl (pz*) silanes exhibit interesting inter- and intramolecular exchange phenomena. Intermolecular reactions involving Si-N vs. Si-Cl dismutation cause equilibria between the three species $Cl_2Si(pz^*)_2$, $ClSi(pz^*)_3$ (main component) and $Si(pz^*)_4$. Intramolecular exchange is interpreted as a "dangling" of the pz*-moieties in every pyrazolyl silane molecule itself.[1]

These phenomena were investigated with one and two dimensional NMR spectroscopic methods at variable temperatures. The "dangling" of the pz*-moieties is slowed down with decreasing temperature and are best visible in the spectra recorded at -40°C. The use of ^1H-^{29}Si-HMBC spectroscopy (heteronuclear multiple bond correlation) allows to assign the olefinic protons to the corresponding silicon species. In the EXSY (exchange spectroscopy) spectra the exchange between the pz*-methyl groups and the NOE (nuclear overhauser effect) correlation between the methyl groups and the olefinic protons are observed at the same time in one spectrum.

The data obtained with EXSY and HMBC-spectroscopy in combination with variable temperature ^1H NMR allows qualitative conclusions concerning the rate of exchange and the dependence on the silicon corresponding species.

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Keywords: *Silanes; NMR spectroscopy; Exchange interactions;*

P-0220

NEW FE(II) PINCER HYDRIDE COMPLEXES AND THEIR APPLICATION IN HYDROGENATION REACTIONS

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Hydrogenation for reducing ketones to alcohols is a common and often used reaction in modern synthetic organic chemistry. Particularly the stereoselective synthesis of enantiopure alcohols is an important topic and usually catalysts based on precious metals, like ruthenium, iridium or rhodium are used. Well defined iron complexes with similar reactivity would provide an excellent alternative, due to the high natural abundance, low costs and low toxicity.

We here report the synthesis, characterization and reactivity of Fe(II) Complexes and their application in hydrogenation reactions. The complexes are based on PNP pincer type ligands with a pyridine or pyrimidine ring with a P-N bond.[1] All ligands are accessible in modular fashion based on simple synthetic methodologies. A useful feature of these ligands is that steric, electronic, and even stereochemical parameters can be manipulated by modifications of the phosphino R groups and the substituents at the aromatic backbone in order to control the reactivity at the metal center.

The ligands are reacted with FeX_2 (X=Cl, Br) in the presence of CO and a silver salt to get a bis-CO PNP precatalyst of the type $[Fe(PNP)(CO)_2Cl]^+$. The CO co-ligand is essential in order to keep the iron center in a low-spin state throughout the catalytic cycle as revealed by DFT calculations. Reduction with elemental Zn yields the catalytic active mono-hydride species.

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Keywords: *homogeneous catalysis; hydrogenation; iron; Density functional calculations;*

P-0221

SYNTHESIS AND CHARACTERIZATION OF NOVEL WATER SOLUBLE PHTHALOCYANINES BEARING TRIFLUOROMETHYLQUINOLINE GROUPS

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Phthalocyanine (Pc) compounds are a very important class of organic materials. They possess a conjugated system of π-electrons and exhibit the ability to chelate metal ions at the center of the ring. The properties of phthalocyanines are influced both by the nature of substituents on the ligand and by the nature of the metal ion in the inner core. Phthalocyanines have found widespread applications in various areas including printing inks, catalysts, display devices, chemical sensors, non-linear optical devices, data storage systems, liquid crystalline charge carriers and second generation photosensitizers for photodynamic therapy .[1–3] Recently, fluorinated metallophthalocyanines (MPcs) are receiving a great deal of attention due to their interesting electron-transfer and photosensitizing properties.[4]

In the present work, we have synthesized novel water soluble quarternized metal free,zinc and indium phthalocyanines including trifluoromethylquinoline substituents on the peripheral positions. The structure of synthesized complexes were characterized by ^{1}H-NMR, UV-Vis, FT-IR and Mass spectroscopic techniques.

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Keywords: *Phthalocyanines; Indium; Zinc; Solubility; Quinoline;*

P-0222

THE ROAD FROM RODS TO CHELATE CARBENE COMPLEXES OF CHROMIUM AND TUNGSTEN ON THIENYL TYPE LIGANDS

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Known chelate carbene complexes are subject to the available reactivity of the chosen ligand[1]. This has been favourable for the synthesis of many mono and biscarbene complexes, but not chelate Fischer carbene complexes, making them extremely rare compared to N-heterocyclic chelate carbene complexes[2–3]. Reaction of dilithiated thiophene species, (2,5-$Li_2C_4H_2S$) with $W(CO)_6$ and subsequent alkylation afforded the known thienyl monocarbene complex and the novel biscarbene complex. To prepare chelated carbene complexes the ligand must be modified to divert reactivity to neighbouring carbon atoms. For this purpose, two options have been suggested: Blocking and activation (or a combination of both). Blocking an α-position on thiophene with a methyl substituent (2-C_4H_3(Me)S) and reacting with two equivalents *n*-BuLi, gave the monocarbene and the unstable methylene biscarbene complex. Monocarbene complexes and the targeted 2,3-thienyl biscarbene chelated complexes were obtained from a lithium-halogen exchange reaction of 3-bromo-5-methylthiophene. Alternatively, the reaction of di(thiophen-2-yl)methane (DTM) with two equivalents *n*-BuLi afforded the di(thiophen-2-ylene)methane biscarbene rods, as the only isolated products. Blocking both 3 and 4 positions on a thiophene ligand, the desired chelated biscarbene complexes were accessible only from 2,3-dibromobenzo[3,2-*b*]thiophene, while lithiation of benzo[3,2-*b*]thiophene (C_8H_6S) only gave the known benzothienyl monocarbene. Modification of the blocking group allows for the reaction of dilithiated 4-methyl-4*H*-thieno[3,2-*b*]pyrrole (C_6H_4N(Me)S) species with $[M(CO)_6]$ to afford the monocarbene complex, the dimetal biscarbene rod and the monometal biscarbene chelated complex, after subsequent alkylation.

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Keywords: *Carbene; Chelate; Reactivity;*

P-0223

NOVEL GREEN-EMITTING IRIDIUM(III) COMPLEXES BASED ON 2-(2,3,4-TRIFLUOROPHENYL)PYRIDINE FOR SOLUTION-PROCESSED ORGANIC LIGHT-EMITTING DIODES

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In the past decades, organic light-emitting diodes (OLEDs) based on phosphorescent complexes have attracted increasing attention. Many OLEDs have been fabricated by thermal evaporation of several organic layers, making the fabrication process relatively complicated and expensive. However, solution processed OLEDs proved satisfactory alternative to those processed by vacuum deposition due to their significantly reduced production cost[1].

We synthesized three phosphorescent iridium(III) complexes based on 2-(2,3,4-trifluorophenyl)pyridine, and their structures and luminescent properties were characterized for solution-processed PhOLEDs; $(tfppy)_2Ir(pic)$ (**1**), $(tfpmpy)_2Ir(pic)$ (**2**) and$(tfpCF_3py)_2Ir(pic)$ (**3**), where tfppy = 2-(2',3',4'-trifluorophenyl)pyridine, tfpmpy = 2-(2',3',4'-trifluorophenyl)-5-(methyl)pyridine, $tfpCF_3py$ = 2-(2',3',4'-trifluorophenyl)-5-(trifluoromethyl)pyridine and pic = picolinic acid. The complexes exhibited photoluminescence peaks at 486, 482 and 513 nm and quantum yields of 19, 18 and 27 % in solution for complexes **1**, **2** and **3**, respectively. Complex **(1)** exhibited a red shift emission compared to Firpic, indicating that the conjugation effect of the 3-position –F atom was significant and led to an increase of HOMO energy level. 3–Substituted CH_3 group in pyridine caused a blue-shift in emission whereas a red-shift was observed for 2–CF_3 substituted pyridine resulting from the change of LUMO energy level due to the electronic effect in pyridine ring. The solution-processed PhOLED performance of complexes **(1), (2), (3)** showed CIE coordinates of (0.18, 0.47), (0.18, 0.47), (0.29, 0.62), maximum external quantum efficiency of 8.48, 6.76 and 7.23% and luminance efficiency of 21.18, 16.66 and 25.43 cd/A respectively.

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Keywords: *iridium(III) complex;*

P-0224

TETRACHLORIDOCUPRATES(II) – SYNTHESIS AND ELECTRON PARAMAGNETIC RESONANCE (EPR) SPECTROSCOPY

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Ionic liquids (ILs) based on metal containing anions and/or cations are of interest for a variety of technical applications, e.g. synthesis of (nano)particles, magnetic or thermochromic materials.

We present the synthesis and the results of electron paramagnetic resonance (EPR) spectroscopic analyses of a series of some new potential ionic liquids on the basis of tetrachloridocuprates(II), $[CuCl_4]^{2-}$, with different sterically demanding cations, e.g. hexadecyltrimethylammonium, tetradecyltrimethylammonium, tetrabutylammonium and benzyltriethylammonium. The cations in this series were used to achieve a reasonable separation of the paramagnetic Cu(II) centers for EPR spectroscopy because this method is very suitable for investigation of paramagnetic copper complexes in different physical states (as solids and as liquids). The spectra are all of axial symmetry but the hyperfine structure was not resolved. This is due to the exchange broadening, resulting from still incomplete separation of the paramagnetic Cu(II) ions. Nevertheless, the principal main values of the electron Zeemann g-tensor (g_{parallel} and $g_{\text{perpendicular}}$) of the complex anions could be determined.

Even though the solid substances show slightly different colors, the UV/Vis spectra of the solutions (acetonitrile) are nearly identical, indicating no structural changes of the tetrachloridocuprate moieties. In contrast the X-ray structures of this type of complexes give a proof of structural differences in crystalline state.

The complexes have a promising potential, e.g. as high temperature ionic liquids, as precursors for the formation of copper chloride particles or as catalytic paramagnetic ionic liquids .[1]

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Keywords: *Cuprates; Ionic Liquids;*

P-0225

USING MELEM AS NUCLEOPHILIC REAGENT TO FORM CYCLIC IMIDES

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Melem $C_6N_7(NH_2)_3$ is one of the most important starting materials for the synthesis of tri-*s*-triazines. In these reactions, melem is usually attacked nucleophilically, e.g. to form melonates[1] or cyamelurates.[2] In literature, reactions describing the amino groups of melem as a nucleophil are rare. With formaldehyde it gives a methanol derivative[3] and with PCl_5 iminophosphoranes are formed.[4]

The current study presents the use of melem as nucleophilic reagent towards carbonyl compounds, e.g. to form cyclic imides. In detail, reactions with phthalic and pyromellitic derivatives were carried out in different solvents and as solid state reaction to access new types of monomeric and polymeric heptazine based triimides.

The monomer exhibits a planar molecular structure as indicated by crystal structure analysis and interesting properties such as high chemical and thermal stability up to 500 °C and remarkable photoluminescence at 500 nm.

These properties provide new targets and prospects using melem as a reagent towards other strong electrophiles.

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Keywords: *Heterocycles; Luminescence; X-ray diffraction;*

P-0226

CONTROLED METAL-METAL COMMUNICATION IN FERROCENYL CARBENE COMPLEXES

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Fischer carbene complexes of the type $[M(CO)_5{=}CFc(OEt)]$ (Fc = ferrocenyl; M = Cr, W) has been reported.Little is known on the electrochemical behavior of these complexes[1]. Ambiguity regarding the extent of M-M communication remains[2, 3]. Cyclovoltammetric studies were performed on a range of ferrocenyl carbene complexes, exhibiting in all cases, except $[Mn(CO)_2{=}CFc(NHBu)]$, quasi electrochemical reversible one electron oxidations of the central metal (Cr, Mn) and at least one oxidation for Fe^{2+}/Fe^{3+}. These well resolved peaks had separations of more than 400mV. Thus charges on the metal centres remain localized. For $[Mn(CO)_2{=}CFc(NHBu)]$, the Mn and Fc peaks overlapped implying charges on the oxidized metal centres are delocalized. Aminolysis to yield this complex was done to investigate the greater donating ability of the amino-substituent. Increased contribution of its resonance structure in the ground state is expected and π-back donation from the Mn towards the carbene carbon is inhibited.The isolation of $[M(CO)_5{=}CFc(OEt)]^+[PF_6]^-$, was achieved by chemical oxidation.Controlled electron flow is useful in molecular switches and nanotechnology for application in molecular computers[4]. Utilisation of this property in directing the site of activity in this type of molecules is being explored in our laboratories.

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P-0227

SPIN-CROSSOVER IRON(II) COMPLEXES WITH A PHOTOACTIVE DIARYLETHENE-BASED LIGAND

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Innovative materials whose magnetic properties can be switched reversibly by light irradiation at room temperature on a single molecular level offer a variety of applications, e.g. as high-density memory units or photoswitches.

The light controlled spin-change in spin-crossover (SCO) metal complexes is well examined as Light-Induced Excited Spin State Trapping (LIESST) effect, with the disadvantage of low operating temperatures (< 50 K).[1] To overcome this limitation we use the recently introduced Ligand-Driven Light-Induced Spin Change (LD-LISC) effect.[2] By utilizing the photoisomerizable diarylethene-based ligand 5,6-bis(2,5-dimethylthiophen-3-yl)-1,10-phenanthroline (**L**)[3] coordinated to an iron(II) center we intend to change the spin state of the metal ion at room temperature via photocyclisation/-cycloreversion of the photoactive ligand. Auxiliary ligands are used to adjust the ligand field strength favourable for a spin transition.

The synthesis, characterisation and photophysical properties of two photoactive Fe^{II} complexes $[Fe(NCS)_2\mathbf{L}_2]$ and $[Fe(H_2B(pz)_2)_2\mathbf{L}]$ ($H_2B(pz)_2^-$ = dihydobis(pyrazolyl)borate) will be presented.

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Keywords: *Spin crossover; Molecular devices; Photochemistry; Magnetic properties; Iron;*

P-0228

FACILE C-S, C-SE AND C-P CROSS-COUPLING REACTIONS IN A WELL-DEFINED ARYL-CUIII COMPLEX. MECHANISTIC IMPLICATIONS IN ULLMANN CONDENSATIONS

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Recent efforts to recover the usefulness of copper in cross-coupling catalysis has led to the implementation of Ullmann chemistry in the construction of C-heteroatom bonds.[1] In the last decade, the exploration of new copper catalysis protocols have proved utility for the formation of C-S, C-Se and C-P bonds.[2] Although catalytic methods have been extensively investigated for these type of reactions, their mechanism is still under debate. This work aims at shedding light into the mechanism of copper-catalyzed cross-coupling reactions using sulphur, selenium and phosphorus-based nucleophiles. Studies conducted with a well-defined aryl-Cu^{III} complex revealed the capability of this complex to undergo aryl-S, aryl-Se and aryl-P reductive elimination to yield biaryl thioethers, aryl alkyl thioethers, biaryl selenide and aryl alkyl phosphonates upon reaction with thiophenols, alkyl thiols, selenols and dialkyl phosphites. Experimental data reveals a p*Ka* and coordination ability dependence on the reaction rates. Competition experiments using bifunctional substrates showed the selectivity of the complex towards thiol functionality in presence of an alcohol in substituted aromatic rings. The implication of Cu^{I}/Cu^{III} redox cycles of these C-S, C-Se and C-P bond-forming reactions are further assessed by the excellent performance of the catalytic version of the reactions. Our results support a mechanistic proposal involving a Cu^{I}/Cu^{III} oxidative addition and reductive elimination type of mechanism for aryl-S, aryl-Se and aryl-P bond formation catalysis.[3]

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Keywords: *Copper; Cross-coupling; C-S; C-Se; C-P bond forming reactions; Ullmann-Goldberg mechanisms;*

P-0229

FORMATION OF PHOTOCHEMICALLY ACTIVE ZNO FILMS ON ALUMINIUM SUBSTRATES BY HYDROTHERMAL TREATMENT

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ZnO is a wide-band-gap semiconductor which has attracted considerable attention over recent years due to its potential applications in solar cells, flat-panel displays, photovoltaic devices and conductive composites. Aluminium is one of the most widely used metals because of its light weight, ease of handling and inexpensive price. Although aluminium has high conductivity, it is difficult to use aluminium as a substrate for photo- or electro-active devices because of the ease with which an insulating surface oxide is formed in atmosphere. Therefore, there is potential for low cost devices if active films such as ZnO can be deposited in intimate contact with aluminium substrates.

In this study, thin ZnO films were formed on the surface of an aluminium substrate by a hydrothermal treatment method utilising an intermediate layered hydroxide. The thermal treatment conditions were optimized by changing the solution pH and reaction temperature. Characterization of the thin ZnO films was carried out by XANES, XRD, XPS, SEM and photocurrent measurement. Photoactive devices were successfully fabricated with the highest photocurrents observed from ZnO films formed under hydrothermal treatment conditions of 383 K and a solution pH of 8.0.

Keywords: *zinc oxide; photocatalysis;*

P-0230

PREPARATION OF MESOPOROUS CATALYSTS FOR OLEFIN METATHESIS

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Olefin metathesis has become a powerful tool in organic synthesis and isnow extremely useful having numerous applications in fine chemicalsynthesis. Ru based complexes are themost popular metathesis catalysts due to their high activity and tolerance to thevariety of functional groups in substrate molecule.Mesoporous molecular sieves are siliceous materials withwell-defined regular architecture, large surface areas, large void volumes andnarrow pore size distribution of mesopores. They represent progressive supports for newheterogeneous catalysts for olefin metathesis and metathesis polymerization. Immobilization of solublemetathesis catalysts on siliceous molecular sieves promised heterogeneousmetathesis catalysts with high efficiency and low metal leaching.

In the present work the heterogenouscatalysts have been prepared by immobilization ofcommercial Hoveyda-Grubbs 1st generation catalyst on siliceousmesoporous molecular sieves (SBA-15, SBA-16 and MCM-48) of different pore sizeand architecture modified with linkers containing dicyclohexylphosphine (PCy_2)groups. SBA-15 ($S_{BET}=688$ m^2/g, $V=1.1 cm^3/g$, $d=6.9$ nm) is mesoporous silicawith hexagonal symmetry of uniform pores. SBA-16 ($S_{BET}=796$ m^2/g, $V=0.6$ cm^3/g, $d=4.7$ nm)is a mesoporous material with three dimensional cubicarrangement of mesopores. MCM-48 ($S_{BET}=756$ m^2/g,$V=0.9$ cm^3/g, $d=6.2$ nm) is a mesoporoussieve with two independent interwoven three-dimensional channels. These catalystsshows low Ru leaching and can be used repeatedly. Filtration tests proved that the activity ofthe catalysts is bound to the solid phase. Effect of the architectureof the supports on catalyst activity (decrease in the order SBA-15 > MCM-48> SBA-16) was observed for the ring closing metathesis of various modelsubstrates (diethyl diallylmalonate, 1,7-octadiene, tert butyl-N, N-diallylcarbamate and N, N-Diallyl-2,2,2-trifluoro-acetamide)(Scheme 1).

Keywords: *olefin metathesis; mesoporous molecular sieves; heterogenous catalysts;*

P-0231

NOVEL SUPRAMOLECULAR PHOTOCATALYSTS BASED ON NHC-LIGANDS

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Supramolecular photocatalysts can play an important role in converting sunlight into usable energy. Current promising examples consist of a ruthenium polypyridyl moiety which is linked to a catalytic centre such as Pd or Pt via a bridging ligand.

The activity of these catalysts depends on their stability throughout the catalytic cycle. One main deactivation mechanism is the release of low-valent metal species observed by Hammarstroem *et al*. in a bridged ruthenium-palladium-system[1] and in other related systems.[2]

However, optimised system stability might be achieved by designing different coordination motifs suppressing bond cleavage between N-donor ligands and these catalyst centres. Here we introduce a new type of bridged system possessing N-heterocyclic carbene (NHC) ligands as anchoring sites for low-valent catalyst species. Related NHC-ligands have recently been used to gain precise control over the electronic and steric properties of catalytic intermediates.[3,4]

Here we present a series of bimetallic complexes where a Ru-centre is connected to a low-valent catalytic centre via an N,N-coordinated 1,3-substituted-1H-imidazo[4,5-f] bridge. The compounds were successfully used as hydrogen evolving catalysts and were fully characterised by spectroscopic and electrochemical studies.[5] Detailed investigations into the synthesis and spectroscopic properties are shown by NMR spectroscopy, absorption and emission measurements indicating the successful preparation of mono- and dinuclear compounds.

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Keywords: *ruthenium; photocatalysis; NHC ligands; hydrogen production;*

P-0232

THE METAL-BINDING SITES OF SUGAR AMINO ACIDS

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Sugar amino acids are carbohydrates containing at least one carboxyl and one amino group at a sugar core. Based on the exchangeable arrangement of the amino and carboxyl group at the sugar core, many different derivatives can be synthesized. Various types of sugar amino acids can also be found in biological systems. There, their extraordinary abilities were utilized in a variety of ways. For example, *N*-acetyl neuraminic acid often represents the last sugar unit in many glycoproteins of higher organisms. Furthermore, some derivatives of *N*-acetyl neuraminic acid play a decisive role in viral infections.

However, the coordination chemistry of these important biomolecules has not yet been investigated satisfactorily. Through the study of the complexes, specific rules of metalation should be proposed. In the last years many $Pd^{II}N_2$-complexes (N_2 = bidentate nitrogen ligand) with carbohydrates were studied and characterized by NMR spectroscopy and single crystal X-ray diffraction. To probe the metal-binding sites of sugar amino acids we used the well analyzed Pd^{II} reagents Pd-tmen (tmen = *N*,*N*,*N'*,*N'*-tetramethylethane-1,2-diamine) and Pd-chxn (chxn = (1*R*,2*R*)-cyclohexane-1,2-diamine) in aqueous solution. Within this poster 2-amino-2-deoxy-gluconic acids are in the centre of attention. Therefore, three sugar amino acids were investigated as representatives for 2-amino-2-deoxy-gluconic acids: D-glucosaminic acid, sodium 2-amino-2-deoxy-D-mannonate and sodium 2-amino-2-deoxy-D-idonate. The sugar amino acids sodium 2-amino-2-deoxy-D-mannonate and sodium 2-amino-2-deoxy-D-idonate were synthesized in a six-step synthesis each. D-Glucosaminic acid was commercially available.

The pH value proved to be a decisive parameter to address the binding sites of sugar amino acids. Hence, the pH was thoroughly controlled in the course of the experiments. Moreover, di- and trimetallation of the carbohydrate was achieved by increasing the concentration of Pd^{II} reagent. The molecular structures were assigned by a combined ^1H-^{13}C-NMR-spectroscopic approach and by single crystal X-ray diffraction.

Keywords: *Coordination modes; Palladium; Carbohydrates; NMR spectroscopy; X-ray diffraction;*

P-0233

ALIPHATIC C–H BOND OXIDATION OF TOLUENE USING ROOM TEMPERATURE STABLE COPPER PEROXO COMPLEXES

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The activation of dioxygen by copper proteins and enzymes plays an important role for catalytic oxidation reactions in nature. Various mononuclear copper complexes have been synthesized as model compounds due to their potential to mimic the active site and the function of such copper proteins and enzymes.[1] The copper(I) complexes of tetradentate tripodal ligands showed the formation of thermally labile dinuclear copper peroxo complexes, $[Cu_2(L)_2(O_2)]^{2+}$, in the presence of dioxygen.[2] These compounds have been investigated for their possible application as catalysts for the selective catalytic oxidation of organic substrates.

In 2009 Lucas *et al.* and Würtele *et al.* demonstrated aliphatic C-H-bond oxidation in the oxidation of toluene to benzaldehyde using copper peroxo complexes with tetradentate tripodal ligands. In these studies the oxidative transfer of oxygen was limited to a stoichiometric conversion up to 40 %.[3, 4]

Recently we succeeded to exceed the limited conversion and to obtain a catalytic oxidation of toluene to benzaldehyde within 30 catalytic cycles. The investigations on aliphatic C-H-bond oxidation reactions were carried out systematically with a series of copper peroxo complexes, $[Cu_2(L)_2(O_2)](BPh_4)_2$ (L = tetradentate tripodal ligand, Tris(2-pyridylmethyl)amine, 2-(Dimethylaminoethyl)bis(2-pyridylmethyl)-amine, Bis(2-dimethyl-aminoethyl)(2-pyridylmethyl)amine, Tris(2-dimethylaminoethyl)amine), that are stable at room temperature.

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Keywords: *Copper; Oxidation; Tripodal ligands;*

P-0234

SIZE MATTERS – INFLUENCE OF NANOPARTICLE SIZE IN THEPERFORMANCE OF MO-SUPPORTED EPOXIDATION CATALYSTS

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Nanochemisty is an exponentially growing research field in modern science that involves the synthesis and application of nanoparticles of different sizes and shapes. Fabrication of core-shell magnetic particles has recently been subject of extensive research, since such materials combine the unique magnetic properties of the core together with the possibility to further functionalize the research. This has motivated research to develop designed application in different fields like bioseparation, drug delivery, MRI, catalysis and others[1]. The specific advantages of magnetic nanomaterials include high specific surface area, active sites mainly distributed on the "outer" surface of the support which avoids pore diffusion and the application of an external magnetic field enables the removal of the particles in a simple way[1].

In the present work we used iron magnetic nanoparticles with different sizes. The particles were subsequently coated with a dense silica layer yielding binding sites (Si-OH units) for heterogenization of molecular catalysts[1]. The core/shell nanoparticles were derivatized with benzoic acid-4-diphenylphosphine and isonicotinic acid, both suitable for coordination of metal centers. This latter step was accomplished by adding the Mo precursor complex $[MoI_2(CO)_3(NCMe)_2]$, yielding the desired magnetic nanocatalysts. All synthesized materials were characterized by adequate spectroscopic techniques (FTIR and DRUV) or other techniques (XRD, Mössbauer and SEM/TEM).

The resulting catalysts were tested in oxidation catalysis, namely, epoxidation of olefins and allylic alcohols, with *t*-butylhydroperoxide.

The results demonstrate that the supported Mo materials are efficient recyclable catalysts for selective olefin epoxidation and reveal that the systems are completely selective for epoxides across several substrates. The reaction conditions (temperature and solvent) and nanoparticles size were found to influence catalysts performance, and will be discussed.

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Keywords: *Nanoparticles; Epoxidation; Molybdenum; Magnetic properties; Heterogeneous catalysis;*

P-0235

D-GLYCOSYLAMINES AND THEIR COORDINATION CHEMISTRY

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Amino sugars are carbohydrates in which one or more hydroxy functions are substituted by an amino group. They occur in nature, for example, in antibiotics, in glycoproteins and in chitin. The latter is built up of β-1,4-linked *N*-acetyl glucosamine molecules and appears in the exoskeleton of arthropods. In this work, the glycosylamines (1-amino-1-deoxy-glycoses) are at the centre of attention. Since amino sugars are potential ligands but there is little known about their features, it is important to acquire more information about this substance group. By studying these complexes, specific rules of metalation can be proposed.

Since glycosylamines are reducing sugars, the four different anomers, β-pyranose, α-pyranose, β-furanose and α-furanose may be accessible for metal chelation. In this poster D-ribosylamine, D-galactosylamine and D-lyxosylamine were discussed as representatives of the group of D-glycosylamines. To present the chelating properties of D-galactosylamine, the reactions with palladium(II) and cobalt(III) were analysed. It is evident that the reactions with the Pd^{II}(tmen) metal fragment [tmen=*N*,*N*,*N′*,*N′*-tetramethylethane-1,2-diamine] and the Co^{III}(tren) metal fragment [tren=tris-(2-aminoethyl)-amine] led to only one species in which the amino sugar binds through its N1 and O2 atoms and exists in the $^4C_1$-β anomer. Moreover, the first crystal structure of a cobalt complex with an unsubstituted D-glycosylamine was obtained. In contrast to these results, the reactions of D-lyxosylamine with Pd^{II}(tmen) and K_2PtCl_4 showed a change in the configuration of the amino sugar. Here, too, the 1-amino function reliably participated in metal binding but the $^4C_1$-β pyranose educt was transformed to its $^1C_4$-α anomer.

Keywords: *NMR spectroscopy; Coordination modes; Conformation analysis; Palladium; Cobalt;*

P-0236

INFLUENCE OF CARBOXYLIC ACIDS ON THE FORMATION OF MIXED- METAL OXO- CLUSTER FROM METAL ALKOXIDES

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Molecular metal oxo- cluster can act as building blocks in inorganic-organic hybrid materials. Strong chemical bonds between the components demand reactive sites on the surface of the cluster, which serve as connectors. In order to achieve highly ordered networks, the geometry of these functional ligands is crucial.

The introduction of oxo- cluster containing two different metals opens the field to an even larger variety of building blocks with different physical and chemical properties. Due to the different bonding characteristics of the used metals and the asymmetric shape of the clusters an anisotropic functionalization can be possibly achieved.

There are several ways to synthesise oxo- cluster, one is to start from the corresponding metal alkoxides and react them with carboxylic acids. The type of cluster formed during the reaction is mainly influenced by the type of alkoxides and acids used, as well as on the alkoxide/acid ratio. In this work, we present the influence of different carboxylic acids on the formation of mixed Ti/Zr oxo- cluster.

Keywords: *cluster compound; Carboxylic acids; X-ray diffraction;*

P-0237

A3B TYPE FLUORINATED UNSYMMETRICAL PHTHALOCYANINES FOR PDT APPLICATIONS

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Phthalocyanines are versatile molecules used as industrial pigments, and they have been applied in a number of applications: for example, photodynamic therapy, photovoltaic devices, catalysts, gas sensors, electrochromic displays and photovoltaic devices. Phthalocyanines have strong absorption at short and long wavelength ends of the visible spectrum and are thus well suited for optical applications. The optical and electrical properties of phthalocyanines can be tuned by changing the center metal and the peripheral substituents. For instance, the fluorescence and phosphorescence quantum yields and the corresponding lifetimes of singlet and triplet states of phthalocyanines depend on their structure. Unsymmetrically substituted phthalocyanines are usually prepared by three principal synthetic strategies: the polymer support route, the subphthalocyanine route, and the statistical condensation route. The most common method is the statistical condensation of two differently substituted dinitriles or diiminoisoindolines (using different ratios 3:1, 6:1, 9:1 etc..) followed by chromatographic separation of the resulting mixture.

In the present work, we describe the synthesize and characterization of A_3B type novel unsymmetrically substituted metallophthalocyanine which has been synthesized by statistical condensation of a mixture of sulfur containing phthalonitrile (A) and fluorinated phthalonitrile (B). The structures of all these compounds were identified by using IR, UV-VIS, ^1H NMR and elemental analyses spectroscopic data.

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Keywords: *PDT application; Unsymmetrical Phthalocyanine; Fluorinated;*

P-0238

PLAYING WITH FE(II) LIGAND FIELD, THE EXAMPLE OF (PYRAZOLYL)PYRIDINE-TYPE LIGANDS: DIMERIC COMPLEXES AND THEIR SPIN-CROSSOVER BEHAVIOUR

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From its discovery in the 1930's till now, spin crossover has been the subject of extensive applications. One of the problems remaining is the ability to organize at will spin crossover systems with the desired properties, since spin crossover remains an elusive property very much depending on the surroundings of the metallic center.

In this context, a very interesting family is the bis(pyrazolyl)pyridine one. With these analogues of the widely-used terpyridine system, many of their homoleptic complexes show spin crossover behaviour [1]. It has also been shown in our laboratory that many complexes can be photoconverted at low temperatures, with long lifetimes of photoexcited high-spin state [2a, b]. They constitute thus interesting building blocks for the obtention of organized systems.

During the course of our present investigations of functionalized subunits of the kind, we have also looked at the possibility of controlling the coordination behaviour of bis(pyrazolyl)pyridine ligands through the use of blocking ancillary ligands. This poster will show the results we have found with pseudohalogens in particular thiocyanate and selenocyanate.

This leads to complex having one free coordination site so the choice of an appropriate ligand either monodentate or bridging bidentate allows to obtain both mononuclear and dinuclear species. Characterization, magnetic and photomagnetic properties of synthesized complexes will be discussed.

Keywords: *iron(II); spin crossover; magnetism; complexes;*

P-0239

PIGGYBACKING FISCHER CARBENE COMPLEXES

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Fischer carbene complexes play an important role in many organic reactions.[1] There are numerous examples of transition metals that can accommodate alkoxycarbene ligands[2], however there is also a wide range of transition metals that form carbene complexes that are difficult to isolate and also metals that do not readily form Fischer carbene complexes. Examples of multimetal Fischer carbene complexes have been synthesized where the role of the metal fragments was investigated for structural features and communication between metal fragments.[3, 4]

In this study the main aim was to transfer Fischer carbene complexes as substituents on a phosphine or amine ligand into the coordination spheres of a variety of transition metals. The substrates chosen: tri(4-bromophenyl)amine and tri(2-furyl)phosphine, are able to accommodate more than one Fischer carbene complex as substituents and also act as very good ligands to a variety of transition metals. The newly synthesized carbene containing complexes of Group 6 to 10 transition metals display interesting spectroscopic and structural features. The study further entails examining the effect the carbene has on the bonding ability of the ligand and also the metal to which the ligand is coordinated. Further investigations will demonstrate the potential of the newly formed complexes which may display catalytic properties or play significant roles in template reactions.

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Keywords: *Fischer carbene complex; Multimetal complex; Ligand coordination;*

P-0240

BISMUTH VANADIUM OXIDE CLUSTERS WITH VISIBLE-LIGHT PHOTOACTIVITY

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Polyoxometalates (POMs) are anionic metal oxo clusters with applications in various fields of research on catalysis[1] and photocatalysis[2]. Structure and reactivity tuning can be achieved by incorporation of heterometal centers like into the cluster shell. In the present study, we were exploring the incorporation of bismuth(III) centers into polyoxovanadates as a potential route for the assembly of vanadates with photoactivity in the visible range.

The idea is based on literature reports which show that solid-state bismuth vanadium oxides are promising visible-light photocatalysts.[3] However, thus far, no molecular analogues of solid-state bismuth vanadate are known. Here, we present the syntheses, characterization and photochemical activities of molecular bismuth vanadium oxide clusters. Structural analyses show that the bismuth vanadate clusters, $H_3[(Bi(dmso)_3)_4V_{13}O_{40}]$ x *ca.* 4 DMSO and $TBA[(Bi(dmso)_3)_2V_{12}O_{33}X]$, are formed around a central, tetrahedral ortho-vanadate VO_4^{3-} or halide ($X=Cl^-$, Br^-), template.[4] One of the main features of bismuth vanadium oxides is their visible-light photoactivity. For these bismuth vanadium clusters, UV-Vis spectroscopy showed a strong O?M LMCT transition; tailing of the LMCT transitions into the visible range up to *ca.* $l=600$ nm is observed. In order to study the visible-light induced photoreactivity of bismuth vanadium clusters, the dye photodegradation of a model pollutant was chosen as a test reaction. The results of the photochemical test reactions as well as the catalytic performance (TON, TOF, quantum efficiency) are discussed in this presentation.

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Keywords: *Photochemistry; Sustainable Chemistry; Vanadium; Catalysis;*

P-0241

BUILDING BLOCKS AND NEW LIGANDS IN CHEMISTRY OF PALLADIUM POLYNUCLEAR CARBOXYLATE COMPLEXES

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Synthesis of platinum metal polynuclear compounds is one of the main challenges in modern cluster chemistry, first of all, due to its unique catalytic properties. Our investigations permitted to identify building blocks for polynuclear palladium carboxylate complexes with coordinated CO and NO.

It was shown that interaction of palladium carbonyl carboxylate clusters $Pd_6(\mu\text{-}CO)_6(\mu\text{-}RCO_2)_6$ (**1**) with gaseous NO leads to formation of 8-nuclear clusters $Pd_8(\mu\text{-}CO)_4(\mu\text{-}RCO_2)_{8\text{-}}(\mu\text{-}NO_2)_4$ (**2**) with nitrite ligands. Clusters **1** and **2** contain 4-nuclear structure unit $Pd_4(\mu\text{-}CO)_2(\mu\text{-}RCO_2)_4$, which was also fixed as $Pd_4(\mu\text{-}CO)_2(\mu\text{-}NO)(\mu\text{-}RCO_2)_5$ (**3**) complexes obtained in the same reaction under the presence of excess of corresponding carboxylic acid. Comparison of structural and spectral parameters for clusters **1-3** allows to conclude that $Pd_4(\mu\text{-}CO)_2(\mu\text{-}RCO_2)_4$ is high-stable unit which can be considered as building block for palladium carbonyl carboxylate clusters. Another feature of the reaction is a formation of nitrite ligands directly from NO.

A building block containing NO was identified when studying reaction of $Pd_4(NO)_2(RCO_2)_6$ (**4**) with acetonitrile. New 5-nuclear complexes of a general formula $Pd_5(CH_3C(=N)OC(=N)CH_3)(NO_2)_x(NO)(RCO_2)_{7-x}$ ($x=0$, 1) (**5**) were obtained in the reaction. Structural and spectral parameters of $Pd_4(\mu\text{-}RCO_2)_5(\mu\text{-}NO)$ unit in complexes **3-5** are very close, so the unit can be considered as building block for palladium nitrosyl carboxylate clusters. Complexes **5** contain a specific ligand – acetamide anhydride. This ligand forms under reaction conditions from acetonitrile as a result of acetonitrile hydrolysis followed by coupling of molecules of acetamide and acetonitrile or two molecules of acetamide.

Finally, studying ESI-mass-spectra of complexes **2** and **3** we have detected $Pd_3(\mu\text{-}CO)_2(\mu\text{-}RCO_2)_2$ units, which later were found in the biggest palladium carboxylate cluster $Pd_{12}(\mu\text{-}CO)_8(\mu\text{-}NO_2)_8(\mu\text{-}RCO_2)_8$ (**6**). Up to date this the first cluster composed of 3-nuclear carbonyl carboxylate metal chains.

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Keywords: *palladium; carbonyl; nitrosyl; nitrite; carboxylate;*

P-0242

CROSS-LINKING OF TWO-DIMENSIONAL METAL CYANIDE NETWORKSBY SOL-GEL PROCESSING

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Ni^{2+} complexes with certain nitrogen-containing organic ligands and various metal cyanides form two-dimensional honeycomb-like analogues of Prussian Blue. The organic ligands block the four equatorial coordination sites of Ni^{2+} and thereby favour this geometrical structure.

So far, attention has mainly been directed at networks of $[Ni(cyclam)]^{2+}$ (cyclam = 1,4,8,11-tetraazacyclotetradecane) with $Fe(CN)_6^{3-}$ [1, 2] or $W(CN)_8^{3-}$ [3, 4]. Research has been focused on them because they possess interesting magnetic properties and microporosity. This combination leads to their classification as “magnetic sponges” [5], which denotes materials that change their magnetic behaviour when the solvent guest molecules are removed.

We are investigating whether the magnetic properties of the materials change upon embedding the two-dimensional sheet structures in an amorphous gel. This is done by cross-linking the layers by means of trialkoxysilylalkyl groups, which are introduced by derivatising the organic blocking ligands, followed by sol-gel processing. The obtained gels are analysed regarding their structure (NMR, spectroscopic measurements, elemental analysis) as well as functionality (magnetic susceptibility, conductivity).

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Keywords: *cyanides; Magnetic properties; microporous materials; Nickel; macrocyclic ligands;*

P-0243

SYNTHESIS, CHARACTERIZATION AND ANTIPROLIFERATIVE ACTIVITY OF SOME TRANSITION METAL COMPLEXES WITH 3-(2-(4-METHOXYPHENYLCARBAMOTHIOYL)HYDRAZINYL)-3-OXO-N-(THIAZOL-2-YL)PROPANAMIDE

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The coordination chemistry of nitrogen-sulfur donor ligands such as thiazole derivatives as well as their transition metal complexes are well documented to have antifungal and antibacterial properties, beside antitumor activity. The aim of this work is to prepare and characterize a new thiazole ligand 3-(2-(4-methoxyphenylcarbamothioyl)hydrazinyl)-3-oxo-N-(thiazol-2-yl)propanamide $\mathbf{H_4L}$ and its complexes and to study its antitumor activity against the human breast cancer cell line (MCF-7). $\mathbf{H_4L}$ structure was confirmed by elemental analysis, IR, mass and ^1H NMR spectroscopy. $\mathbf{H_4L}$ complexes with Cu(II), V(IV), Co(II), Mn(II) and Ni(II) have been characterized by elemental analyses, molar conductivities, spectral (UV-Vis, IR, ^1H NMR, mass) as well as magnetic moment measurements technique. The IR spectra suggest that H_4L acts as a uni-negative tetradentate or mono-anionic bidentate ligand. The molar conductance measurements proved that all complexes are non-electrolytes, except **Ni, Co** and **Cu**complexes behaved as electrolytes. The results revealed that the complexes possess a tetrahedral, square planar, square-pyramidal or octahedral geometry. The newly synthesized complexes have been tested for their antibacterial and antitumor activities. The effect of the new compounds on proliferation of human breast adenocarcinoma cell line MCF-7 showed that all studied compounds have anticancer activity except **Co** and **V** complexes, where the synthesized complexes have antitumor activity values more than that of the free ligand. The smaller value of IC50 of **Ni** complex than that of the cisplatin would provide a new potential antitumor drug.

Keywords: *transition metal complexes; antiproliferative activity; thiazol derivatives;*

P-0244

COORDINATION COMPLEXES OF GALLIUM: A WAY TO OVERCOME ANTIMICROBIAL RESISTANCE?

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The World Health Organization (WHO) has identified the growing resistance of microbes to known antimicrobial drugs as one of the greatest threats to human health, because it hampers the control of infectious diseases, threatens a return to the pre-antibiotic era and jeopardizes the achievements of modern medicine; in addition, it increases global health care costs[1]. New antimicrobial agents that target new biological sites of action are needed to overcome the antimicrobial resistance.

One potential target is iron metabolism. Iron is critical for the metabolism and growth of most organisms, and many animal species, including humans, limit the availability of iron at the site of infection as a mechanism of host defense[2]. Ga^{3+} shares many chemical similarities with Fe^{3+}, which makes it difficult for biological systems to distinguish the two metals; however, the 3+/2+ redox chemistry essential for the iron metabolism cannot be accessed for gallium, which results in cellular toxicity. Consequently, Ga^{3+} has been stamped as the *Trojan horse* in biological systems[3].

In a bioinorganic chemistry approach to new potential metalloantimicrobials, our group has synthesized gallium(III) complexes of the (fluoro-)quinolones, a class of synthetic broad-spectrum antibiotics. To further explore the structure-activity-relationship of these new potential metalloantimicrobials, the corresponding iron(III) complexes were included in the antimicrobial susceptibility studies to test the *Trojan horse theory*.

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Keywords: *Antibiotics; Bioinorganic Chemistry; Gallium;*

P-0245

MIXED SUGAR-CORE-PHOSPHATE LIGATION OF D-FRUCTOSE 1,6-BISPHOSPHATE WITH THE RE(V)O(TMEN) METAL FRAGMENT

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Sugar phosphates play a decisive role in all organisms. They're ubiquitous in metabolism pathways such as the pentose phosphate pathway or glycolysis. All reactions of these pathways are catalysed by enzymes. Several of these contain divalent metal centres, e.g. magnesium, iron or zinc, in their active site. The dications are chelated by the sugar phosphate substrates during the catalysed reaction. Well known examples for such metalloenzymes are class-II aldolase, fructose 1,6-bisphosphatase and glucose 6-phosphate isomerase. Since crystal structure analyses of enzymes offer only limited results about the initial binding of ground-state sugar-phosphate forms to metal centres, it's necessary to investigate such complexes in aqueous solution outside enzymes.

Sugar phosphates are able to coordinate in various ways to a metal centre whereby the pH is an important parameter. So at alkaline pH values, only the hydroxyl functions of the sugar-core coordinate to the metal centre while, at lower pH values, solely the coordination of the phosphate groups occurs. Close to the physiological pH, another coordination type is possible. In the case of D-fructose 1,6-bisphosphate, a mixed sugar-core-phosphate ligation exhibiting a seven-membered chelate ring is observed in the presence of the metal fragments Pd^{II}(en) and Al^{III}(tacn) (en = ethane-1,2-diamine, tacn = 1,4,7-triazacyclononane). This coordination pattern was also found in the enzyme 3,4-dihydroxy-2-butanone 4-phosphate synthase. However, no crystal structure analysis has been available yet, proving this special coordination type outside an enzyme.

Here we present the results of experiments of the $Re^{V}O$(tmen) metal fragment (tmen = tetramethylethane-1,2-diamine) with D-fructose 1,6-bisphosphate as well as its model glycerol 1-phosphate. It is shown, via both mass and NMR spectroscopy, that with an $Re^{V}O$ metal fragment the formation of a mixed sugar-core–phosphate ligation could be achieved. Moreover, the first crystal structure determination verifying this coordination pattern outside an enzyme can be presented.

Keywords: *Coordination modes; Rhenium; O ligands; NMR spectroscopy; x-ray diffraction;*

P-0246

CHLORIDE AND CARBOXYLATE COMPLEXES OF GOLD(III) WITH N,N-DONOR LIGANDS

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Chemistry of gold complexes is a growing modern area of coordination chemistry. First of all this is due to broadening use of gold compounds in homogeneous catalysis. Analysis of influence of ligands environment is impossible without the information about structure and reactivity of such compounds which makes study of new gold chloride and carboxylate complexes a topical issue.

The general approach to synthesis of gold(III) carboxylate complexes with N,N-donor ligands (2,2'-bipyridine, phenanthroline) is a substitution of chloride ligands in complexes $[LAuCl_2]X$ under action of silver carboxylates. The most common-used starting materials are complexes $[LAuCl_2]Cl$. In order to reduce a consumption of silver carboxylates we changed inner-sphere chloride ions with BF_4^- ions.

Complexes with BF_4^- ions were used as starting materials for reaction with silver acetate, trimethylacetate and trifluoroacetate. The reaction leads to formation of corresponding carboxylate gold(III) compounds $[LAu(RCO_2)_2]BF_4$. According to X-ray diffraction and IR-spectroscopy data they are mononuclear complexes with chelate coordination of N,N-donor ligands and terminal coordination of two carboxylate groups. Complexes are quite stable but slowly decompose under the light. Trifluoroacetates are noticeably less stable than others carboxylates.

Our attempts to substitute chloride ligands in $[(phen)AuCl_2]Cl$ without use of silver carboxylates gave unexpected result. Reaction of $[(phen)AuCl_2]Cl$ with sodium acetate in glacial acetic acid at 80°? leads to essential rearrangement of gold coordination sphere. A half of $[(phen)AuCl_2]^+$ ions lose phenanthroline and join chloride ligands giving $[AuCl_4]^-$ anions. The reaction results in formation of $[(phen)AuCl_2][AuCl_4]$ complex, which was characterized by X-ray diffraction analysis. The quantum-chemical calculations show that $[LAuCl_2][AuCl_4]$ are products of thermodynamic control in the systems $[LAuCl_2]^+–RCO_2^-– Cl^-$ (calculations were carried out for L = 2,2'-bipyridine, phenanthroline and R = CH_3, CMe_3, CF_3).

Acknowledgement: *We are grateful to the Council of the President of the Russian Federation for young scientists for financial support (project 977.2012.3).*

Keywords: *gold; chloride; carboxylate; N,N-donor ligands;*

P-0247

A BIOINSPIRED, INORGANIC OXYGEN EVOLVING CATALYST BASED ON A MANGANESE POLYOXOVANADATE CLUSTER

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Here, we present a bioinspired, novel $[Mn_4V_4O_{17}(OAc)_3]^{3-}$ cluster (= {Mn4V4}) which features a central manganese-oxo cubane $[Mn_4O_4]^{6+}$ core supported by four corner-sharing $[VO_4]$ tetrahedra acting as inorganic 'tripodal' ligands. The cubane unit is stabilised by three $[VO_4]$ tetrahedra directly, which are connected to the manganese atoms by six bridging V-O-Mn bonds in total. In addition, three acetate ligands fill the coordination sphere. Compared with other $[Mn_4O_4L_6]$ complexes this $[Mn_4O_4]$-polyoxovanadate unit is air-stable and easily accessible.

The four manganese centres were tentatively assigned as $Mn^{III}_2Mn^{IV}_2$ based on bond valance sum calculations, elemental analysis and ESI-MS. The cyclic voltammogram of the $\{Mn_4V_4\}$ cluster in acetonitrile shows three distinct reversible redox waves (-0,90 V, 0,08 V and 1,07 V) which indicate a highly redox-active species. ESI-mass spectrometry confirmed the existence of the $\{Mn_4V_4\}$ cluster in solution.

This oxygen evolving complex (OEC) model complex is inspired by nature and an aqueous solution of $\{Mn_4V_4\}$ is capable of oxygen evolution in the presence of a stoichiometric oxidant like cerium ammonium nitrate (Ce^{IV}) or light-driven by a well-known Ru-based system ($[Ru(bpy)_3]Cl_2$ / $S_2O_8^{2-}$).

Since these are our initial results we have to optimise the system and to improve the turnover numbers. Furthermore, the exact redox-reactions of the manganese-oxo core needs to be investigated. In addition, it has to be shown that the reaction is indeed homogeneous and does not involve the formation of heterogeneous particles.

Keywords: *Polyoxometalates; Oxygen evolving complex; Manganese; Vanadates; Oxygen evolution;*

P-0248

BRIDGING PSEUDOHALIDES IN PALLADACYCLES AS SOURCE OF DIFFERENT ASSEMBLIES

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Background and Objectives: Following our previous studies on the reactivity of (piperidinomethyl)silylmethyl cyclopalladated complexes, we decided to explore the behavior of this soft metallic center containing two coordinative sites available in cis geometry toward pseudohalides such as cyanide, thiocyanate or azide, which present several possible coordination modes and may give rise to different assemblies.

Results: The reaction of $[Pd\{CH_2SiPh_2(CH2NC5H10)$-$k^2C,N\}(m\text{-}Cl)]_2$ ($CH_2NC_5H_{10}$=piperidinomethyl) with KSCN leads to the centrosymmetric dimer $[Pd\{CH_2SiPh_2(CH_2NC_5H_{10})$-$k^2C,N\}(m\text{-}SCN\text{-}k^1S,k^1N)]_2$, which features side-on bridging thiocyanate ligands. The analogous reaction with NaN_3 yields the dimer $[Pd\{CH_2SiPh_2(CH_2NC_5H_{10})\text{-}k^2C,N\}(m\text{-}N_3\text{-}k^1k^1N)]_2$, in which the azide ligands exhibit end-on coordination. This complex persists as a mixture of cis and trans isomers in solution. Lastly, the square tetrametallic complex $[Pd\{CH_2SiPh_2(CH_2NC_5H_{10})\text{-}k^2C,N\}(m\text{-}CN\text{-}k^1C,k^1N)]_4$, is obtained from the reaction between the parent chloride-bridged complex and AgCN. In solution, this compound displays an equilibrium between tetrametallic and trimetallic species. Thermodynamic data were determined, showing that the formation of the trimetallic isomer is thermodynamically disfavored and that the variation of the enthalpy and entropy are positive.

Conclusions: Bridging azide and bridging thiocyanate give rise to bimetallic species where azide is coordinated end-on, and thiocyanate as side-on. In contrast, linear bridging cyanide gives rise to a square shaped tetrametallic complex. The latter is in equilibrium with a trimetallic isomer in solution while the bridging azide dimer persists as a mixture of cis and trans isomers in solution. The trimetallic species is always the minor isomer, and its ratio increases with dilution of the solution, with increasing temperature, and with increase in polarity of the solvent used.

Keywords: *Self-assembly; Metallacycles; Silanes; Bridging ligands;*

P-0249

16 COBALT(II)-CONTAINING HETEROPOLYTUNGSTATE SINGLE-MOLECULE MAGNETS

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Polyoxometalates (POMs) are a large class of discrete, anionic metal-oxides comprising early transition metals in high oxidation states, such as W^{VI}, Mo^{VI}, V^{V}.[1] There has been increasing interest in this field due to potential applications of POMs in various fields including catalysis, magnetism, medicine, materials science, and chemical analysis.[2] Lacunary heteropolytungstates allow for incorporation of transition metal ions, potentially resulting in species with high nuclearity magnetic cores.[3]

Very recently, we reported on the 16 Co^{II}-containing $[(PW_9O_{34})_4\{Co^{II}{}_4(OH)_3PO_4\}_4]^{28-}$ ($\mathbf{Co_{16}\text{-}PW_9}$), composed of four Keggin-type $\{Co_3PW_9\}$ fragments encapsulating a central $\{Co_4O_4\}$ cubane unit, which in addition is capped by four external phosphate groups, resulting overall in a polyanion with idealized T_d point group symmetry (see Fig. 1).[4] We have now succeeded in preparing $[(SiW_9O_{34})_4\{Co^{II}{}_4(OH)_3PO_4\}_4]^{32-}$ ($\mathbf{Co_{16}\text{-}SiW_9}$) and $[(GeW_9O_{34})_4\{Co^{II}{}_4(OH)_3PO_4\}_4]^{32-}$ ($\mathbf{Co_{16\text{-}}GeW_9}$), the isostructural silicon and germanium analogues of $\mathbf{Co_{16}\text{-}PW_9}$ in a simple, one-pot procedure by reacting the trilacunary $[A\text{-}a\text{-}SiW_9O_{34}]^{10-}$ or $[A\text{-}a\text{-}GeW_9O_{34}]^{10-}$ with Co^{II} ions in phosphate buffer. These polyanions were investigated in the solid state by single-crystal XRD, FT-IR spectroscopy, thermogravimetric and elemental analyses.

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P-0250

COMPUTATIONAL STUDY OF SUBSTITUENT EFFECT IN PARA SUBSTITUTED PLATINABENZENE COMPLEXES

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The electronic structure and properties of the platinabenzene and *para* substituted platinabenzenes have been investigated using the hybrid density functional mpw1pw91 theory. The substituent effect in structure parameters, frontier orbital energies, aromaticity indexes, and hyperpolarizability has been study. The calculations show that HOMO®LUMO transition has most contribution in t the most intense electronic transition for all molecules.

Keywords: *Platinabenzene; substituent effect; hyperpolarizability; Nucleus-independent chemical shift (NICS);*

P-0251

SYNTHESIS, CHARACTERIZATION, PHOTOPHYSICAL, PHOTOCHEMICAL AND AGGREGATION BEHAVIOR OF 4-[2-(1,4-DIOXA-8-AZASPIRO[4.5]DEC-8-YL)ETHOXY-SUBSTITUTED PHTHALOCYANINES

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Phthalocyanines (Pcs) are the most interesting materials because of their highly conjugatedπ-electron system and chemical stability. They are used extensively in biological and technological areas such as chemical sensors, liquid crystals, catalysis, non-linear optics and photodynamic therapy (PDT) of cancer [1].

The novel treatment is PDT in cancer therapies. PDT is based on a photochemical reaction, which is initiated by light activation of a photosensitizing drug causing tumour cell death. Light is mainly applied by superficial illumination of the tumour and the surrounding tissue causing drug activation followed by tumour cell death. Phthalocyanines (Pcs) and metallophthalocyanines (MPcs) are useful photosensitizers due to their intense absorbtion in red region of the visible light [2, 3].

In this study, the novel metal-free (**4**)and zinc (II) (**5**) phthalocyanine compounds substituted with four 1-(2-hydroxyethyl)-4-piperidone ethylene ketal functional groups at peripherally positions have been prepared. These new phthalocyanine compounds have been characterized by IR, ^{1}H NMR, ^{13}CNMR spectroscopy, MS spectra data and elemental analysis. The synthesized phthalocyanine compounds exhibited excellent solubility in common organic solvents and the zinc (II) phthalocyanine complex (**5**) showed J-type aggregation in chloroform. The photophysical and photochemical properties of metal-free (**4**) and zinc (II) (**5**) phthalocyanine complexes were also investigated in DMSO. The investigation of the photophysical and photochemical properties of photosensitizers is very useful for photodynamic therapy (PDT) applications.

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Keywords: *Phthalocyanine; Aggregation; Photodynamic therapy; Zinc; Singlet oxygen;*

P-0252

SYNTHESIS AND CHARACTERIZATION OF CO(II) PHTHALOCYANINE AND INVESTIGATION OF ITS CATALYTIC ACTIVITIY ON ALCOHOL OXIDATION

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Catalytic oxidation of alcohols is of great importance for the manufacture of fragrances and many synthetic intermediates for organic synthesis [1, 2]. Traditional methods for performing such a transformation involve the use of stoichiometric quantities of heavy inorganic oxidants, such as chromium(VI) or permanganate, which are toxic and pose significant environmental problems. Hence, the development of efficient and environment-friendly catalysts for alcohol oxidation using oxygen source has attracted great research interest. Many researchers have reported the use of highly active metallic catalysts for the alcohol oxidation [3].

Metallophthalocyanine complexes especially Co(II) phthalocyanines are readily available oxidation catalysts and found to transfer oxygen from various oxygen donors to alcohols, alkanes, alkenes, phenols and thiols in numerous studies [4]. Herein, we report the synthesis and characterization of {2-[3-(diethylamino)phenoxy]ethoxy} group substituted Co(II) phthalocyanines and the catalytic behavior of these complexes in oxidation of alcohol.

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Keywords: *Phthalocyanine; Cobalt; Catalysis; Oxidation;*

P-0253

SYNTHESIS, CHARACTERIZATION AND CATALYTIC ACTIVITIY ON CYCLOHEXENE OXIDATION OF PERIPHERALLY TETRA-SUBSTITUTED COBALT(II) PHTHALOCYANINE

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Phthalocyanines (Pcs), a family of aromatic macrocycles based on an extensive delocalized 18-p electron system, have been extensively studied due to their unique optical, electronic, catalytic and structural properties.[1] The catalytic conversion of alcohols in to their corresponding carbonyl compounds is an important reaction in organic synthesis. Syntheticmetalloporphyrins have been investigated extensively as models for the activity of cytochrome P-450 [1].

In this work, we have synthesized and characterized of new cobalt(II) phthalocyanine substituted with four 3,3-diphenylpropoxy groups. The new compound was characterized by IR, UV-Vis, elementel analysis and MS spectral data. This cobalt complex was investigated as catalyst for cyclohexene oxidation with TBHP, m-CPBA and H_2O_2 as an oxidant in organic solvent (DMF). Tert-butylhydroperoxide was found to be the best oxidant for cyclohexene oxidation since higher conversion and selectivity were observed when this oxidant was used.

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Keywords: *Phthalocyanine; Cobalt; Synthesis; Cyclohexene oxidation; Oxidant;*

P-0254

PERIPHERAL AND NON-PERIPHERAL TETRA-SUBSTITUTED WATER SOLUBLE ZINC(II) PHTHALOCYANINES: SYNTHESIS, PHOTOPHYSICS AND PHOTOCHEMISTRY

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Phthalocyanines (Pcs), a family of aromatic macrocycles based on an extensive delocalized 18 p electron system, have been extensively studied due to their unique optical, electronic, catalytic and structural properties. Owing to their strong and long-wavelength absorptions, high efficiency at generating reactive oxygen species and ease of chemical modification, phthalocyanines have emerged as a promising class of second-generation photosensitizers for photodynamic therapy (PDT) [1–4]. Over the last decade, a substantial number of phthalocyanine-based photosensitizers have been prepared and evaluated for their photodynamic activity, with focus on zinc, silicon and aluminium analogues as a result of their desirable photophysical properties.

In this study, we report on the synthesis, characterization and spectroscopic behaviour as well as photophysical (fluorescence quantum yields and lifetimes) and photochemical (singlet oxygen and photodegradation quantum yields) properties of zinc phthalocyanine complexes substituted with four {2-[3-(dimethylamino)phenoxy]ethoxy} groups on both peripherally and non-peripherally positions.

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Keywords: *Phthalocyanine; Zinc; Quaternization; Photodynamic therapy; Photosensitizer;*

P-0255

PHOTOCHEMICAL FATE- THE LOCALIZATION OF THE INITIAL ELECTRONIC TRANSITION DETERMINES THE EFFICIENCY OF CATALYTIC ACTION IN SUPRAMOLECULAR PHOTOCATALYST

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Artificial photosynthesis presents a promising solution to the looming energy crisis by converting sunlight into chemical fuels. In particular, supramolecular photocatalysts present an interesting class of substances in this context. These systems allow for synthetic optimization of the intramolecular energy- and electron-transfer processes by local modifications of the ligand architecture.

In this contribution we discuss the photophysics and photocatalysis of the supramolecular photocatalyst **RuPd** (Bis-(4,4'-di-tert-butyl-2,2'-bipyridine)–ruthenium(II)-μ (tetra-pyrido[3,2-a:2,3'c:3",2",-h:2'",-3'"-j]-phenazine)-dichloro-palla-dium(II)).- The combination of various spectroscopic techniques yields a detailed picture of the photoinduced processes in **RuPd** and structurally related model systems. The dynamic range of the joint use of resonance Raman, femtosecond time-resolved transient absorptions and luminescence spectroscopy covers timescales of several orders of magnitude. Based on detailed spectroscopic characterization we shall discuss the correlation of the photoinduced excited-state dynamics with the catalytical efficiency of the **RuPd** system and its dependence on structural modifications of the ligand architecture. Based on the spectroscopic results presented, we shall discuss a novel concept for the design of artificial photosynthetic systems, which is based on tailoring the properties of the Franck-Condon point of absorption.

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Keywords: *artificial photosynthesis; photophysics; photochemical hydrogen evolution; electron transfer;*

P-0256

REDOX DIRECTED PROCESSES IN THE DESIGN OF NOVEL NANOSCALE HETEROPOLYACIDS

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Polyoxometalates (POMs) are an exciting class of discrete metal-oxygen cage complexes with a tremendous variety of structures, compositions and properties.[1]. In this work we decided to explore the use of oxidizing agents such as sodium chromate in the synthesis of novel lanthanide containing tungstoarsenates. In particular, when using the trilacunary lone-pair-containing $[As^{III}W_9O_{33}]^{9-}$ as the POM precursor, there is a partial *in-situ oxidation of the* As^{III} *heteroatom* of the POM precursor, leading to a large mixed-valent AsIII/AsV polyanions with formula $[Ln_{12}As^{III}_8As^{V}_2W_{90}O_{328}(H_2O)_{36}(OAc)_4]^{48-}$ (Ln = Gd^{III}, Tb^{III}, Dy^{III}, Ho^{III} Er^{III}, Tm^{III}, Yb^{III}, Lu^{III}). The same reaction conditions in presence of cerium(III) ions lead to in-situ oxidation of Ce^{III} ions to Ce^{IV}followed by a self-assembly into the novel tetrameric polyanion $[Ce^{IV}_4As^{III}_4W_{41}O_{149}]^{24-}$.

Keywords: *polyoxometalate; self-assembly; in-situ oxidation; lanthanoids; tungstoarsenate;*

P-0257

LITHIATED SULFOXIDES – ALPHA-SULFINYL FUNCTIONALIZED CARBANIONS

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α-Heteroatom functionalized alkyl lithium compounds of the type $LiCHRYR'_n$ (Y = N, P, O, S, Cl, …) exhibit a unique reactivity; thus, for example, those with electronegative groups YR'_n may react as carbenoids.[1] A further point of interest is the configurational stability of the carbanionic C atoms.[2] Sulfur functionalized lithium compounds, among them lithiated sulfoxides Li[CRR'S(O)R''], have been hardly investigated in this respect.[3–5] In the present work, lithiated sulfoxides of the type $[Li_2\{CRR'S(O)Ph\}_2(TMEDA)_2]$ (**I**) were obtained by direct metallation of the respective sulfoxides with *n*-BuLi/TMEDA. In the solid state, in type **I** compounds, no Li–C interactions were recognized; thus, there is a "free" α-carbanionic center having a planar configuration (see the structural image with R/R' = Me/Me as example). The dynamics of type **I** lithium compounds in solution was investigated by low-temperature NMR measurements and, moreover, these results were confirmed by DFT calculations. Furthermore, here we report on reactions of type **I** compounds with various electrophiles and their diastereoselectivity as well as on the decomposition of type **I** compounds exhibiting a carbenoid reactivity.

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Keywords: *carbanion; carbenoid; lithiated sulfoxide;*

P-0258

DENSITY FUNCTIONAL THEORY STUDY OF THE DELTAHEDRAL DICOBALTADICARBABORANES HAVING NINE TO TWELVE VERTICES

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The basic building blocks of metal-free polyhedral boranes and isoelectronic carboranes have long been recognized to be the most spherical deltahedra, also known as closo deltahedra. Vertex atoms in the deltahedral dicarbaborane $C_2B_{n-2}H_n$ structures can be replaced with isolobal transition metal units leading to very stable metalladicarbaboranes and dimetalladicarbaboranes. Compounds having CpCo (Cp=η^5-C_5H_5) vertices in place of BH vertices in carborane structures are of particular interest since CpCo vertices, as formal donors of two skeletal electrons, are isolobal with BH vertices. The theoretical predictions from this study agree well with experimental data on the numerous known $Cp_2Co_2C_2B_{n-4}H_{n-2}$ (n=9, 10, 11, and 12) derivatives. The lowest energy structures for the dicobaltadicarbaboranes $Cp_2Co_2C_2B_{n-4}H_{n-2}$ (n=9, 10, and 11) are found by density functional theory to be the most spherical borane deltahedra with the carbon atoms at degree 4 vertices and the cobalt atoms at degree 5 or 6 vertices. Thus for the nine-vertex $Cp_2Co_2C_2B_5H_7$ system only the two lowest energy isomers are found experimentally; these lie within 3 kcal/mol of each other and ~6 kcal/mol below the next lowest energy isomer. For the ten-vertex $Cp_2Co_2C_2B_6H_8$ system three of the six lowest energy isomers are known. The 11-vertex $Cp_2Co_2C_2B_7H_9$ systems provide examples of stable high energy isomers with direct Co–Co or C–C bonds arising from the synthetic methods used. Thus one of the experimentally known 11-vertex Cp2Co2C2B7H9 isomers is a high-energy structure with adjacent carbon atoms lying ~26 kcal/mol above the global minimum. For the icosahedral 12 vertex dicobaltadicarbaboranes $Cp_2Co_2C_2B_8H_{10}$ with only degree 5 vertices, the lowest energy structures are those without Co–Co or C–C edges.

Keywords: *metallaboranes; cobalt; density functional theory;*

P-0259

FROM BISMUTH OXIDO CLUSTERS TO METASTABLE SS-BI$_2$O$_3$ NANOPARTICLES SHOWING HIGH PHOTOCATALYTIC ACTIVITY

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Bismuth oxides are interesting materials in terms of their environmentally benign, non-toxic behavior and interesting properties.[1] For example α-Bi_2O_3/Bi_2O_4 nanocomposites are excellent photocatalysts and δ-Bi_2O_3 exhibits high oxide ionic conductivity.[2-4] However, controlled synthesis of metastable bismuth(III) oxides is difficult as a result of a distinctive polymorphism. Six different polymorphs are known until now. α-Bi_2O_3 with its monoclinic structure is stable at room temperature. Upon heating it is transformed into the cubic δ phase at approximately 730 °C which is stable upon its melting point. On cooling one out of two metastable bismuth(III) oxides, tetragonal β- or cubic γ-Bi_2O_3, is stabilized depending on the reaction conditions. So far factors that control the polymorphism in bismuth(III) oxides are not fully understood. In our approach we use nanoscaled bismuth oxido clusters[5, 6] as model compounds and starting materials for the synthesis of bismuth(III) oxide polymorphs. The clusters show an interesting structural relationship with δ- and β-Bi_2O_3.

Here we present several bismuth oxido clusters such as $[Bi_6O_4(OH)_4(NO_3)_6(H_2O)]\cdot H_2O$,[7] $[Bi_{22}O_{26}(OSiMe_2{}^tBu)_{14}]$,[8] $[Bi_{38}O_{45}(OMc)_{24}(DMSO)_9]\cdot 2DMSO\cdot 7H_2O$[9] (OMc=$O_2CC_3H_5$) and $[Bi_{38}O_{45}(NO_3)_{20}(DMSO)_{28}](NO_3)_4\cdot 4DMSO$.[5] which are promising precursors for the synthesis of metastable β-Bi_2O_3 nanoparticles with high photocatalytic activity in the visible light region. The investigations are supported by *in-situ* X-ray powder diffraction, electrospray mass spectrometry experiments and molecular dynamic simulations which provide insight into the nucleation and decomposition process of bismuth oxido clusters to give bismuth oxides. Furthermore, UV-Vis spectroscopy, transmission and scanning electron microscopy and nitrogen adsorption measurements were used for the characterization of the β-Bi_2O_3 nanoparticles.

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Keywords: *bismuth oxido cluster; bismuth oxide;*

photocatalysis; nanoparticles; metastable phases;

Poster session 1 - Inorganic Chemistry

P-0260

ANTIPYRINE COMPLEXES OF RARE EARTH IODIDES AND PERCHLORATES: STRUCTURE AND PROPERTIES

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Antipyrine (2,3-dimethyl-1-phenyl-3-pyrazolin-5-one, AP) and its derivatives have been widely used as analgesic, antipyretic and anti-inflammatory drugs, their biological activity being attributed to its scavenging activity against reactive oxygen and nitrogen species and to the inhibition of neutrophil's oxidative burst [1]. It was found [2] that metal complexes generally have a better activity than free ligands.

The title compounds $[Ln(AP)_6]X_3$ ($X = I^-, ClO_4^-$, Ln = La-Nd, Sm-Lu, Sc, Y) have been synthesized and studied. It was demonstrated that the complexes form two isostructural series of respective iodides and perchlorates. On the basis of the single crystal XRD and IR spectra studies it was found that the central atom coordinates antipyrine molecules via the oxygen atom of carbonyl group, the iodide-or perchlorate ions being in the outer sphere. The complexes are characterized by the presence of the intracomplex $\pi - \pi$ stacking interaction, the phenyl rings being almost parallel to the five-membered pyrazole rings of the AP molecules from the adjacent sectors. IR spectra (Calculated using all-electron relativistic DFT-PBE approach) were in good agreement with the experimental ones.

Cytotoxicity of the complexes was studied using the mouse fibroblasts NCTN clone L929 cells and the Hep-2 epithelial cells. It was found that $[Ln(AP)_6]I_3$ at approximately equal molar concentrations inhibit the NCTC clone L929 cell survivability in more extent than antipyrine. The non-monotonous dependences of the cells survivability on the atomic number Z of the central complex-forming lanthanoid atom is observed by comparison of the complexes cytotoxicity with respect to the cells of both types. Perchlorate complexes demonstrated a more pronounced inhibiting effect in comparison with the iodide ones.

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Keywords: *Rare Earths; X-ray diffraction; Quantum Chemistry; Cytotoxicity;*

P-0261

BIS-C-PIVOT LARIAT ETHERS: SYNTHESES, SPECTROSCOPIC PROPERTIES AND STEREOCHEMISTRY OF 15-18-MEMBERED CORONANDS WITH TWO DIALKYL PHOSPHONATE GROUPS

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A large number of methods for the preparation of diverse α-aminoalkylphosphonates, in which the carboxylic acid group [C(O)(OH)] is replaced by a phosphonate group $[P(O)(OR)_2]$, have been published since the first synthesis by Fields in 1952 but, the most convenient is the nucleophilic addition of dialkyl phosphites to the C=N bonds of Schiff bases. This synthetic route was followed in the synthesis of the *bis*-C-pivot macrocycles containing both phosphonate and amine functionalities in the same molecule, $(CH_2)_3\{o\text{-}CH[P(O)(OR)_2]NHPhO\}_2X$, using dimethyl phosphite $[HP(O)(OCH_3)_2]$ and diethyl phosphite $[HP(O)(OC_2H_5)_2]$ with the dibenzo-*bis*-imino crown ethers $\{(CH_2)_3[o\text{-}CH{=}NHPhO]_2X$; X:$-CH_2CH_2-$, $-CH_2CH_2CH_2-$, $-CH_2CH_2CH_2CH_2-$ and $-CH_2CH_2OCH_2CH_2-\}$ in dry MeOH. The nucleophilic addition of dimethyl or diethyl phosphite to CH=N bonds in dibenzo-bis-imino crown ethers is of paramount importance in providing tetra-substituted carbon atom, [CH(phosphonate)(amine)(arom)], which is a centre of chirality and as each macrocycle contains two equivalent chiral carbon atoms then the molecules are expected to be diastereoisomers and exist in *meso* and *racemic* forms. The structures of the compounds have been characterized by elemental analysis, FTIR, MS and NMR measurements. ^1H, ^{13}C and ^{31}P NMR assignments have been made for the *meso* and *racemic* forms of *bis*-C-pivot macrocycles by analysis of chemical shifts, signal intensities, spin-spin coupling constants, splitting patterns and 2D HETCOR NMR techniques. Due to the presence of two chiral carbon centres, *bis*-C-pivot macrocycles can be valuable to be investigated as bioactive molecules and pharmacological agents. The synthesized *bis*-C-pivot macrocycles may serve as a potential new class of supramolecular host molecules because of their natures to give rise to intermolecular hydrogen bonds confirmed by X-ray crystallography. The phosphorylation addition reaction to dibenzo-*bis*-imino crown ethers produces adjacent N–H and P=O moieties in the molecule with the potential of parallel orientation, and hence of forming a pair of antiparallel hydrogen bonds with a similar grouping on a second molecule.

Keywords: *Macrocycles; Schiff Bases; NMR Spectroscopy; Diastereoselectivity; X-ray Difraction;*

P-0262

MULTINUCLEAR MANGANESE-CONTAINING POLYOXOTUNGSTATES:SYNTHESIS, STRUCTURE, AND CATALYTIC CAPACITY

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Inorganic compounds are generally known to be formed from atoms of a metallic nature as their intrinsic building units. Polyoxometalates (POMs) are discrete, nano-sized metal-oxo anions of high oxidation state early transition metals, predominantly V^V, Nb^V, Ta^V, Mo^{VI}, and W^{VI}.[1a] They are adaptable structures with natural properties in nano-sized dimensions, shape, charge density and surface reactivity due to the flexibility of their chemical composition, charge, and counterions.[1] Such properties render POMs highly desirable for magnetic, electronic, and catalytic studies amongst others.[2, 3]

Polyanions containing several paramagnetic *d*-block ions are of interest for oxidation catalysis applications. In particular manganese-containing polyanions are important here, and very recently our group has reported the synthesis and magnetic properties of a new member, the Mn_{19}-containing polyanion $[Mn^{II}_{19}(OH)_{12}(SiW_{10}O_{37})_6]^{34-}$ {$\mathbf{Mn_{19}}$}.[4] To date only a few high-nuclearity, mixed-valence polytungstates have been prepared, usually based on reactions of Mn^{II} and MnO_4^-, or the well-known {$\mathbf{Mn_{12}}$}, with lacunary polytungstate precursors.

We have investigated the reactivity of {$\mathbf{Mn_{12}}$} with lacunary heteropolytungstates. This approach has enabled us to synthesize the polyanions $[Mn^{III}_3(OH)_3(H_2O)_3SiW_9O_{34}]^{4-}$ {$\mathbf{Mn_3}$-Keggin}, $[Mn^{III}_3Mn^{IV}(CH_3COO)_3SiW_9O_{37}]^{6-}$ {$\mathbf{Mn_4}$}, $[Mn^{III}_3(H_2O)_5(PW_9O_{34})_2]^{9-}$ {$\mathbf{Mn_3}$-Knoth}, and $[Mn^{III}_6Mn^{IV}_4O_4(OH)_{12}(H_2O)_{12}(AsW_9O_{34})_4]^{22-}$ {$\mathbf{Mn_{10}}$}, which were all characterized by single-crystal XRD, electrochemical studies, TGA, and IR spectroscopy. These compounds have tremendous potential in electro- and oxidation-catalysis.

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Keywords: *Polyoxometalates; Oxidation; Homogeneous catalysis; Manganese; Magnetic properties;*

P-0263

HIGH-NUCLEARITY, MAGNETIC METAL-OXO ASSEMBLIES STABILIZED BY HETEROPOLYTUNGSTATES

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Lacunary heteropolytungstates are known to act as inorganic multidentate ligands with oxygen atom donors at the lacunary sites.[1] The combination of 3d transition metals with lacunary heteropolutungstates is part of the TMSP (Transition Metal-Substituted Polyoxometalates) subclass. Recently, a growing interest started to show in TMSP's comprising high nuclearity (>10) metal-oxo cage complexes with paramagnetic centers, due to their potential to exhibit Single Molecular Magnet (SMM) behavior.[2] Interaction of the wheel-shaped 48-tungsto-8-phosphate $[H_7P_8W_{48}O_{184}]^{33-}$({$P_8W_{48}$}) with copper(II) and iron (III) formed the 20-copper(II)- and 16-iron(III)-containing species {$Cu_{20}P_8W_{48}$} and {$Fe_{16}P_8W_{48}$} respectively, which correspond to the parent lacunary precursor {P_8W_{48}} encapsulating a $[Cu_{20}Cl(OH)_{24}(H_2O)_{12}]^{9-}$ and a $[Fe_{16}(OH)_{28}(H_2O)_4]^{20+}$ core.[3] Interaction of the trilacunary nonatungstosilicate $[SiW_9O_{34}]^{10-}$ ({SiW_9}) with manganese(II) and its phosphate analogue $[PW_9O_{34}]^{9-}$ ({PW_9}) with cobalt(II) ions in basic phosphate buffer formed the 19-manganese(II)- and 16-cobalt(II)-containing species {$Mn_{19}Si_6W_{60}$} and {$Co_{16}P_4W_{36}$} respectively, corresponding to a sheet-like $[Mn_{19}(OH)_{12}]^{26+}$ core stabilized by six $[SiW_{10}O_{37}]^{10-}$ units and a tetrahedrally arranged $[Co_{16}(OH)_{12}(PO_4)_4]^{8+}$ core stabilized by four {PW_9} units.[4]

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Keywords: *Polyoxometalates; Transition metals; Magnetic properties;*

P-0264

PRE-ORGANZIED METAL ALKOXIDES

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Organically modified metal alkoxides are well known as precursors for sol-gel materials, since substitution of part of the alkoxo groups opens the chance of lowering the reactivity and better controlling of sol-gel processing. To this end, different types of ligands, e.g. ß-diketonates, ß-ketoesterates, amines and oximates can be used. While sol-gel processing of the metal alkoxide complexes results in unstructured materials, pre-organized precursors open the possibility to prepare structured metal oxide-based materials. One access is through polymeric metal alkoxides, which retain their structure during the hydrolysis process, another one can be the formation of MOF-like structures.

First experiments to react titanium alkoxides with bis(ß-ketoesters) and bis(ß-diketones) resulted in cyclic dimeric structures with two bridging ligands and two terminal alkoxides per titanium atom. ESI-MS- and NMR-measurements proved that no polymeric products were formed, as the cyclic dimers seemed to be thermodynamically more stable. Dimeric or oligomeric structures were also obtained with dioximes. As SAXS measurements showed no pre-organization of the precursors, the number of functionalities per ligand was increased to three and four. 1,3,5-Benzene-tri-p-benzoic acid (L_1), adamantane-1,3,5,7--tetracarboxylic acid and others were chosen as ligands.

Reaction of titanium isopropoxide with different proportions of these ligands resulted in insoluble residues, which were characterized by IR, SAXS and XPS. From a ratio of 2:1 (Ti:COOH) a two-dimensional structure was built with L_1. Therefore, using adamantane as the spacer between the four carboxylic groups should open the possibility to form three-dimensional structures. Lower metal alkoxide to ligand ratios resulted in a dense material with no specific pre-structuring. Partial hydrolysis studies and XPS measurements will be performed to check whether the anticipated pre-structure is retained in the hydrolysed materials.

Keywords: *titanium; metal alkoxides; multifunctional ligands;*

P-0265

HIGH NUCLEARITY TRANSITION METAL CONTAINING POLYOXOMETALATES

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Polyoxometalates (POMs) are a large class of discrete, anionic metal-oxides comprised of early transition metals in high-oxidation states, such as W(VI), Mo(VI), or V(V).[1] There has been increasing interest in this field due to potential applications of POMs in various fields including catalysis, magnetism, medicine, materials science, and chemical analysis.[2] Lacunary heteropolytungstates allow for incorporation of transition metals, and in particular POMs containing a high nuclearity magnetic core are of major interest.[3]

Here we report on the 16 Co^{II} containing $[(PW_9O_{34})_4\{Co^{II}_4(OH)_3PO_4\}_4]^{28-}$ which is composed of four Keggin-type $\{Co_3PW_9\}$ fragments encapsulating a central $\{Co_4O_4\}$ cubane unit, which in addition is capped by four external phosphate groups, resulting overall in a polyanion with idealized T_d point group symmetry.[4] The 14 Ni^{II} containing $[(A\text{-}\alpha\text{-}P_2W_{15}O_{56})_4(Ni_{14}\ O_{10}(OH)_6(PO_4)_4]^{58-}$ is composed of four Wells-Dawson type $\{Ni_3P_2W_{15}\}$ fragments encapsulating a central di-nickel-oxo unit and four capping phosphate groups. Both polyanions were synthesized in simple one-pot reactions in aqueous phosphate buffer (pH 8), and structurally characterized in the solid state by single-crystal X-ray diffraction, FT-IR, and TGA.

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Keywords: *Polyoxometalate; magnets; Co; Ni;*

P-0266

X-RAY DIFFRACTION AND IR SPECTROSCOPY FOR NANO-SIZED ITO DOPED WITH SOME METAL OXIDES

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Nanocrystalline indium tin oxide (ITO) doped with 2, 4 and 6 mole % of CuO, Cr_2O_3, and ZrO_2 powder have been synthesized by pechini method. The crystalline structure of all the prepared samples was identified using XRD and IR spectroscopy. The morphology and average grain size of the prepared powder were determined using TEM and XRD. The effect of different dopant, different concentration, dopant cation valence and ionic radius on the crystalline structure, lattice parameter, crystallite size and strain were investigated. All samples have single cubic bixbyite phase structure except ITO samples doped with Zr. They have cubic bixbyite structure as predominant phase and traces of rhombohedral phase. Pure ITO sample has higher lattice parameter value than those of ITO samples doped with ZrO_2 and lower lattice parameter value than those of ITO samples doped with CuO and Cr_2O_3.

Keywords: *Nano-sized doped ITO; Structural properties; IR; TEM;*

P-0267

SOLVOTHERMAL SYNTHESIS OF NEW MAGNETIC MATERIALS BASED ON RHENIUM(IV)

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$ReCl_4L$ (L - aromatic amine) complexes were obtained by solvothermal method in a Berghoff pressure reactor.

The presented product, $ReCl_4$(2,2'-bipyrimidine)·$(CH_3)_2SO_2$, crystallizes in orthorhombic crystal system, a = 18.6257(3), b = 12.9848(3) c = 12.4753(3) ?, V = 3017.16(11) ?^{3}, Z = 4. Intramolecular C-H···Cl hydrogen bonds are present in the complex molecule (C(5)-H(5)···Cl(2): where H···Cl 2.73 ? C···Cl 3.317(3) ?, < CHCl 122°, and C(8)-H(8)···Cl(4) where H···Cl 2.81 ? C···Cl 3.386(3) ?, < CHCl 121°), additionally stabilizing the crystal structure. The magnetic properties were investigated from susceptibility measurements preformed on polycrystalline samples in the temperature range 1.7-300 K. The magnetic behavior found is typical of antiferromagentically coupled systems, and susceptibility maxima are found at 12 K. Short Re-Cl···Cl-Re contacts account for the observed antiferromagnetic behavior.

The study on the coordination chemistry of rhenium and its compounds is of great interest due to several therapeutic, catalytic, photophysical and magnetic properties.

One on first compounds with characterized magnetic properties was $[ReCl_4(py)_2]$ obtained via solvothermal synthesis.[1]

Rhenium(IV) complexes of $ReCl_4L$ (L – aromatic amine) general formula were examined with respect to their anti-tumor properties and they may be applied in treatment of breast, prostate and ovary cancer.[2]

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Keywords: *Rhenium(IV); magnetic materials; solvothermal synthesis.;*

P-0268

[N]SILA-ACENES (N = 2-4): THE INFLUENCE OF RING SIZE ON THE PROPERTIES

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The structure and properties of [n]sila-acenes (n = 2-4) were investigated by density functional theory method. The results of calculations were obtained at B3LYP/6-311G(d,p) level on model species. Energetic criteria suggest that **2-1b (n = 2), 3-1b (n = 3)**, and **4-1b (n = 4)** isomers enjoy stabilization. By frontier orbital analysis, these systems are among the most stable of the family. Also, calculations indicate the most stable isomers have the most first hyperpolarizability values. The aromaticity of all molecules has been studied by nucleus-independent chemical shift.

P-0269

STRUCTURE, MAGNETIC AND ELECTROCHEMICAL PROPERTIES OF $LINI_{1/3}MN_{1/3}CO_{1/3}O_2$ PREPARED VIA CITRATE-GEL METHOD

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Layered $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ oxide was synthesized by citrate gel method with molar ratio Li/M = 1, (M = Ni +Mn +Co). Structural properties studied by X-ray diffraction (XRD) and magnetic measurements carried out by superconducting quantum interference device (SQUID) showed the well-defined a-$NaFeO_2$ structure with cationic distribution close to the nominal formula. 3.2% of nickel ions were located into the Li sublattice as estimated from magnetic measurements. Electrochemical properties were investigated by both potentiostatic and galvanostatic charge-discharge cycling. High capacity values were observed for the prepared oxide from electrochemical measurement. An initial discharge capacity of 176 $mAhg^{-1}$ was delivered at C/15-rate in the cut-off voltage of 2.5–4.5V vs. Li/Li^+. More than 87% of its initial capacity was retained after 35 cycles at C/15-rate.

Keywords: *LiNi1/3Mn1/3Co1/3O2; Li-batteries; squid;*

P-0270

CO_2 REDUCTION UTILISING PHOTO-ELECTRO-CATALYTIC APPROACH BASED ON TRANSITION METAL COMPLEX CATALYSTS ANCHORED TO SEMICONDUCTORS

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A prominent current area of research is that of CO_2 reduction in which CO_2 can be chemically reduced to one of several different chemical feedstocks including methanol and formaldehyde. These feedstocks are of great importance to many sectors of industry and it would be highly beneficial if they could be produced cheaply and efficiently. There are two main approaches to achieving this goal, using electrocatalysts[1] or photocatalysts[2].

Our research is currently focusing on using systems which combine both a semiconductor material and an electrocatalyst in order to reduce CO_2. The semiconductor is a nitrogen doped Ta_2O_5 which acts as a photosensitizer capable of absorbing photons with energies corresponding to the visible region of the spectrum[3]. The electrocatalyst is a transition metal complex with anchoring groups to allow attachment to the semiconductor. Upon photon absorption, the semiconductor generates the necessary potential difference and transfers an electron to the catalyst, which in turn reduces CO_2. We are presently investigating electrocatalysts based on ruthenium and rhenium diimine complexes with two types of anchoring groups, 4,4'-dicarboxylic acid (dcbpy) and 4,4'-diphosphonic acid (dpbpy).

Results from rhenium complexes containing dpbpy anchoring groups will be presented. Initial electrochemical studies suggest that CO_2 reduction indeed occurs using these complexes in an acetonitrile solution at room temperature.

We would like to thank the White Rose university consortium for funding and support.

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Keywords: *Cyclic voltammetry; Photochemistry; Rhenium; Semiconductors;*

P-0271

COPPER(I) COMPLEXES OF ACYCLIC P,N,N',P'-LIGANDS FOR SUSTAINABLE OLED-TYPE DEVICES

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Organic light-emitting devices (OLEDs) based upon transition metal or lanthanide metal emitters or sensitizers have attracted a great deal of attention due to their potential use in lighting as well as future panel display applications[1]. In recent years, copper(I) complexes showed promising results as a sustainable alternative to the traditionally adopted lanthanide emitters or sensitizers and the external quantum efficiency and up to 16% has been realized[2].

With the goal of optimizing light emitting properties of copper(I) complexes, we have synthesized a family of *P,N,N',P'*-type ligands along with their mononuclear copper(I) complexes. The properties of these complexes and structure-property relationships will be presented.

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Keywords: *ligand design; luminescence; copper; N,P ligands;*

P-0272

SYNTHESIS AND CHARACTERIZATION OF NEW PHOSPHASILAPROPENES

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Three new phosphasilapropenes type Mes*P=C(Cl)--SiCl(Ph)R, [R=Cl (**1**), R=9-methylfluorenyl (**2**), R=9-trimethylsilafluorenyl (**3**), Mes*=2, 4, 6-tri-*tert*-butylphenyl] were prepared and completely characterized by physico-chemical methods. Their structure in solid state was confirmed by X-ray diffraction studies on monocrystals. Dichlorophosphasilapropenes **2** and **3** were obtained starting from the trichlorophosphasilapropene **1**. The latter derivatives were synthesized in an attempt to improve the steric protection around the P-C-Si moiety, by replacing one of the chlorine atoms from the silicon atom with the bulkier 9-methylfluorenyl (**2**) or 9-trimethylsilafluorenyl groups (**3**).

The reactivity of phosphasilapropenes is currently under investigation.

Keywords: *phosphasilapropene; multiple bonding;*

P-1017

STRUCTURAL, MECHANISTIC AND CATALYTIC ASPECTS OF COPPER(II) COMPLEXES CONTAINING 2,6-BIS(IMINO)PYRIDYL LIGANDS

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In search for Cu(II) complexes having [$Cu^{II}N_3$] cores as a catechol oxidase model, new five-coordinate trigonal bipyramidal complexes of the type [$Cu^{II}(pyN_3)Cl_2$], with sterically constrained chelate ligands, were synthesized and X-ray structurally characterized. The ligand substitution kinetics for chloride substitution by bio-relevant ligands was studied as a function of nucleophile concentration, temperature and pressure. Catalysis of the oxidation of 3,5-di-tert-butylcatechol to 3,5-di-tert-butylquinone was studied, and correlations between the reactivity, chloride substitution behaviour, and reduction potentials of complexes are reported. The results show that the rate of oxidation is independent of the rate of chloride substitution, indicating that the substitution of chloride by catechol as substrate occurs in a fast step. Spectral data show a non-linear relationship between the ability of the complexes to oxidize 3,5-DTBC and the Lewis acidity of their copper(II) centres. Electrochemical data demonstrate that the most effective complex has an E½ value that approaches the E½ value of the natural tyrosinase enzyme.

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Keywords: *Biomemetics; amine ligands; Catechol oxidases; Crystal structure;*

P-0273

SYNTHESIS OF HIGHER AMINO SUGARS

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A convenient synthesis leading to 2-amino-heptoses and -octoses has been developed. These higher amino sugars, although scarcely known, play important roles in biological systems. Thus, it has been shown that the cell wall LPS of certain bacteria contain 2-amino-heptoses.[1] Furthermore, 2-amino-octodiose, which is formed by oxidation at C-8, is present in the antibiotics Apramycin and Oxyapramycin. However, previous syntheses[2] of octodioses lack a certain amount of stereochemical flexibility, which would be highly interesting in terms of biological activity. The title compounds are prepared starting from the unprotected carbohydrates D-arabinose, D-galactose and D-glucose through a two carbon chain elongation applying the indium mediated allylation strategy.[3] The acetate protected products containing a terminal olefin moiety were ozonized and yielded after base treatment the two carbon chain-elongated, α,β-unsaturated chiral aldehydes. These aldehydes were subsequently stereoselectively epoxidized utilizing a chiral, L-prolin derived catalyst following the JØrgenson's protocol.[4] After transformation of the aldehyde *via* a Wittig reaction to the corresponding α,β-unsaturated-γ,δ-epoxy esters, the epoxide was regio- and stereoselectively opened with an azide nucleophile under palladium catalysis.[5] Full deprotection finally yields the desired higher amino sugars. However, an unexpected side reaction in this respect generated highly functionalized tetrahydrofurane derivatives, which belong to the class of C-glycosides. Through carefully adjusting the reaction conditions, both substance classes are now available. In summary, we developed a simple, highly versatile route for the synthesis of rare, 2-amino functionalized heptoses, octoses and the corresponding methyl acetate C-glycosides respectively.

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Keywords: *Higher Amino Sugars; Indium mediated Allylation; Stereoselective Epoxidation of Enals; Palladium catalyzed Epoxide Opening;*

P-0274

QUADRUPLE CLICK REACTIONS FOR THE SYNTHESIS OF CYSTEINE-TERMINATED LINEAR MULTIBLOCK COPOLYMERS

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More recently, click reactions including the copper--catalyzed azide–alkyne cycloaddition (CuAAC), Diels–Alder, thiol-ene/thiol-yne, and nitroxide radical coupling (NRC) reactions widely adapted to polymer chemistry have emerged as powerful tools for the preparation of multisegmented block copolymers with a wide variety of macromolecular architectures. [1–9]

In this work synthesis of cysteine-terminated linear polystyrene (PS)-b-poly(e-caprolactone) (PCL)-b-poly(methyl methacrylate) (PMMA)/or poly(tert-butyl acrylate)(PtBA)-b--poly(ethylene glycol) (PEG) copolymers was carried out using sequential quadruple click reactions including thiol-ene, copper-catalyzed azide–alkyne cycloaddition (CuAAC), Diels–Alder, and nitroxide radical coupling (NRC) reactions. Because the thiol-ene reaction has its own limitations based on the polymer–polymer conjugation, instead the cysteine molecule was used for conjugation to the polymer blocks. Moreover, this quadruple click combination will be effective to prepare a variety of end-functional polymer blocks from molecules with thiol functionality. Thus, this combination displays a potential strategy in which biomolecule–polymer conjugates (biohybrids) from biomolecules with thiol functionality can be prepared.

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Keywords: *Polymerization; Click chemistry; Polymers;*

P-0275

NEW FLUORESCENT MEMBRANE PROBES: FROM NAPHTHALENEDIIMIDES TO OLIGOTHIOPHENES

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New fluorescent probes are introduced as an innovative methodology to label lipid bilayer membranes. This system is based on the dynamic covalent linkage between a hydrophilic charged head [1] and a fluorescent tail. Dynamic amphiphiles [2] formed from core-substitued naphthalenediimides (cNDIs) and perylenediimides (cPDIs) were tested first. These probes are insensitive to their environment and able to partition selectively into liquid-disordered (Ld) microdomains of mixed lipid bilayers and to activate DNA transporters [3]. These results confirm the potential of dynamic fluorescent amphiphiles to selectively label extra- and intracellular membranes. Oligothiophenes have been selected for the second generation of dynamic fluorescent amphiphiles. Lessons from nature suggest that the combination of fluorophore polarization (push-pull fluorophores) [4, 5] and fluorophore planarization could provide an attractive approach to achieve high sensitivity to membrane fluidity (microdomains), membrane potential and membrane stretching (and interesting NLO properties at interfaces). This combination is explored systematically by varying number and nature of substituents along the oligothiophene scaffold in combination with different donors and acceptors at both ends. Preliminary results in large unilamellar vesicles (LUVs) of variable fluidity are very encouraging.

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P-0276

9-C-SUBSTITUTED PHENALENONES AS PROMISING PRECURSORS FOR THE FORMATION OF NEW STABLE OPEN-SHELL HETEROAROMATICS

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We report the access to a series of new phenalenyl type radicals using 9-C-substituted phenalenones. Phenalenyl radicals are usually arranged in equilibrium between a diamagnetic σ-dimer and a paramagnetic π-dimer. To shift the balance towards the π-dimer, we focus on the practical preparation of π-radicals without steric hindering groups but with electronic effects arising from the incorporation of a heteroatom in the molecular structure. The target compounds have open shell systems, thus they are amphoteric redox species and are able to form both cation and anion with invariant molecular structure. The analysis was carried out using cyclic voltammetry, X-Ray analysis, NMR-, ESR- and UV/Vis-spectroscopy. In the presentation, the syntheses, characterisation, physical properties and the importance of these compounds in modern applications will be presented and discussed.

P-0277

NOVEL THERAPEUTIC AGENTS FOR THE TREATMENT OF RHEUMATOID ARTHRITIS

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The bone tissue is a connective tissue composed of a mineral part, made of calcium phosphate in the form of hydroxyapatite crystals (HA : $Ca_{10}(PO_4)_6(OH)_2$), and of an organic part containing an extracellular matrix and numerous specialized cells (osteoclasts, osteoblasts...).[1] These different components are balanced and every malfunction leads to the appearance of specific pathologies such as osteoporosis which is a disease characterized by an important bone resorption.

Nowadays, different drugs are proposed to treat bone diseases such as **zoledronic acid** (or zoledronate) which is the most efficient anti-resorptive commercialized agent. Its **high activity on bone** is particularly due to the presence of a **Hydroxy-BisPhosphonic acid (HBP) function** which strongly chelate hydroxyapatite crystals.

This efficient binding property of HBPs to the surface of bone makes them potential tools to target bone and deliver various drugs to it.[2] Such a concept could be expressed by the design of **"bifunctional molecules"** where a HBP function is attached to a linker bearing a drug on the other end. In the laboratory, we have recently developed this concept to potentially treat **rheumatoid arthritis** with attachment of **NSAID (Non-Steroidal Anti-Inflammatory Drug)** to the vectors.[3]

This communication will outline **different synthetic routes** to a family of "bifunctional molecules" with the application of a **novel procedure** to access to complex HBPs starting from carboxylic acid precursors.[4]

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Keywords: *biological activity; carboxylic acids; Drug design; phosphorus; inflammation;*

P-0278

FUNCTIONALISED POLYMERS BY SURFACE MODIFICATION USING DIARYL CARBENES

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The use of diaryl diazo compounds for the direct surface modification of polymers is a novel post-polymerisation method, which is suitable for adjustment of the surface characteristics of materials for particular applications, without changing their bulk properties. The project aims to establish an efficient method for the introduction of two classes of organic compounds, namely pyridine-type metal coordinators and spiropyran-type photochomophores, onto materials.

The modified materials with pyridine moiety are developed for ligation with zinc complexes of bis(thiosemicarbazone), or Zn[ATSM]. Upon transmetallation of the Zn(II) complex with radioactive Cu(II), the polymers provide a solution of Cu[ATSM] as a biologically active and hypoxia selective copper-based marker for detection of hypoxia in tumours. The desired diazo compound with a remote pyridine moiety was synthesised and then used for surface modification of polystyrenes. The modified materials were reacted with zinc complexes to demonstrate the ability to coordinate with metals, ligand exchange with Cu(II) gave a solution of copper complexes. HPLC, EPR, and UV/Vis spectroscopy confirmed the existence of copper complexes in the eluent solution.

Spiropyrans are a type of photochromic switch that can be interconverted reversibly between two states upon irradiation at different wavelengths as a result of photocyclisation. The desired photochromic and diazo molecules were independently synthesised, and then coupled prior to surface modification of polymers. An examination of the photochromic properties found that the photoinduced process could be demonstrated by irradiation with UV light, with a significant change in contact angles on modified PET sheet.

These two modifications demonstrate the utility of this approach to introduce diverse macroscopic functions.

Keywords: *surface analysis; synthetic methods; polymers;*

P-0279

3-STYRYLFLAVONES SYNTHESIS: HECK VERSUS WITTIG REACTIONS

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Styrylchromones constitute a small group of natural oxygen heterocyclic compounds. Only 2-styryl-derivatives have been found in nature and these derivatives are also known for their significant biological activities[1]. The interest in 3-styryl-derivatives is growing in the last years and some synthetic methods have been developed[2]. The first report on the synthesis of one 3-styrylflavone consist of a Wittig reaction of a phosphorous ylide, obtained from 3-bromomethylflavone, with benzaldehyde[3]. Recently we reported the synthesis of 3-styrylflavones using the Heck reaction of 3-bromoflavones with styrene derivatives[4]. Having in mind the importance of developing new synthetic approaches towards 3-styrylflavones we design a new efficient route to obtain 3-methylflavones and to use them in a Wittig reaction strategy to obtain 3-styrylflavones. In this communication we will present our results on the synthesis of 3-methylflavone derivatives and the reaction sequence of their transformation into 3-styrylflavones. We will also compare this synthetic route with the Heck reaction one in order to discuss the benefits of each one.

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Keywords: *Wittig reaction; Heck reaction; Halogenation; NMR spectroscopy; Synthetic methods;*

P-0280

SYNTHESIS OF POLY-AZAHETEROAROMATIC LIGANDS AS FOLDAMERS CENTRAL LINKERS FOR AN APPLICATION IN SUPRAMOLECULAR CHEMISTRY

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Polydentate nitrogen ligands represent attractive targets in chemistry/biology/physicochemistry. For many years, Profs. D. Dubreuil and E. Léonel's groups were interested in pyridazinic and pyrrolic compounds particularly for their synthetic methodology and their various applications.[1] Indeed, molecules featuring these heterocycles are present in therapeutic chemistry as anticancer agents (Prodigiosine or metallic complex of cisplatine) and also in supramolecular chemistry as central linkers for the synthesis of foldamers as biological receptor mimics.[2] Our collaborative works with Dr. I. Huc in the field of synthesis and characterization of supramolecular structures led us to elaborate oligoamidic-type foldamers including an azaheteroaromatic ligand as central linker. We have demonstrated their ability to encapsulate diastereoselectively small molecules such as tartaric acid.[3]

Focusing the elaboration of the central linkers, we turned our attention to (poly)-pyridazinic and (poly)-pyrrolic structures. Their preparations are based on various methodologies of C-C bond formation, including electrochemical and chemical cross-coupling processes.

In this communication, the synthetic approach of central linkers will be presented following organometallic chemistry for cross-coupling reactions. Results obtained in supramolecular chemistry will also be discussed.

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Keywords: *Nitrogen heterocycles; C-C coupling; Electrochemistry; Helical structures; Supramolecular chemistry;*

P-0281

PALLADIUM-CATALYZED HETEROCYCLIZATION/REDUCTIVE COUPLING CASCADES OF 2-ALKYNYLBENZAMIDE-TYPE SUBSTRATES AND METHYL VINYL KETONE

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Nucleophile-tethered unsaturated derivatives participate in Pd(II)-catalyzed heterocyclization/reductive coupling reactions with α,β-unsaturated aldehydes and ketones leading to heterocyclic derivatives where the carbonyl compound carbon framework is incorporated as an exocyclic 3-oxopropyl unit.[1] In these reactions, Pd(II) serves a dual role as cyclization and coupling promoter to eventually generate a *C*-palladium enolate, which is finally protonated. Normally, useful reactivity has required the use of excess amounts of halide salts as additives and/or acidic solvents to effectively steer the behavior of the palladium enolate towards protonation rather than β-H elimination, a competing process leading to the alternative Heck products.

We now report the application of this strategy to the use of 2-alkynylbenzamides as novel nucleophilic partners in Pd-catalyzed heterocyclization/reductive coupling cascades with methyl vinyl ketone. In contrast to related applications, these reactions do not require the use of protic solvents or excess halide additives, and proceed effectively under Pd(II) catalysis in the presence of just substoichiometric amounts of added KI or alternatively with the use of PdI_2 as catalyst without any other additive. In this manner, products resulting from 6-*endo*-cyclizations followed by reductive coupling are obtained in 76–97% yields without significant interference from Heck or alternative regiochemical pathways.

High structural diversity is attained in the final products emanating from the choice of alkyl or aryl substituents in the alkyne and nitrogen moieties of the starting 2-alkynylbenzamide, as well as from the possibility of additional structural variations introduced at the benzamide-type aryl ring, including various heterocyclic motifs.

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Keywords: *Palladium; C-C coupling; Cyclization; Heterocycles;*

P-0282

SYNTHESIS OF PRIVILEGED SCAFFOLDS: MIMICKING 1,5-BENZODIAZEPINE-2,4-DIONES VIA A MODULAR APPROACH ON SOLID-PHASE

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Recent developments in modern drug discovery are based on the application of “privileged structures” defined by Evans *et al.* as structures capable of displaying activity towards different receptors[1]. Benzopyrans, diketopiperazines and 1,5-benzodiazepin-2,4-diones are well-known and widely investigated scaffolds, e.g. the latter showing anxiolytic and antiarrhythmic effects. Now, we propose a new potential “privileged structure” containing a 1,5-disubstituted triazole moiety mimicking the *cis*-amide bond within the 1,5-benzodiazepin-2,4-dione motif.[2]

Molecules based on this [1,2,3]-triazolo[1,5-*d*]benzo-1,4-diazepin-2-one scaffold are synthesized and decorated *via* a modular approach on Wang resin using α-amino acids, 2-ethynylaniline or 2-amino-3-ethynylpyridine building blocks and *N*-alkylating agents resulting in five points of diversity. The methodology involves the attachment of α-amino acids onto a solid support, subsequent removal of the Fmoc group followed by an optimized diazotransfer reaction of the resulting amine yielding a resin-bound azide. Conversion of the latter into a 1,5-disubstituted 1,2,3-triazole moiety is achieved quantitatively by addition of a range of 2-ethynylaniline or 2-amino-3-ethynylpyridine building blocks using a Ru(II)-catalyst. The desired scaffold can be obtained in high crude purities (> 95%) in solution *via* an acid catalyzed one-step cyclisation-release strategy. Solution-phase *N*-alkylation finally affords the fully diversified scaffold. In this fashion, several libraries of this [1,2,3]-triazolo[1,5-*d*]benzo-1,4-diazepin-2-one scaffold (62 compounds) have been synthesized in moderate yields by successfully varying all diversity points.

Interestingly, fully diversified compounds exhibit atropoisomeric effects. This fast-slow exchange between two or more conformers can be studied *via* ^1H NMR spectroscopy and therefore more information about the thermodynamics of this scaffold can be revealed.

Taking into account future screening results of the synthesized libraries, a well-thought decoration of this scaffold leading to discovery of new lead molecules is within reach.

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Keywords: *Solid-phase synthesis; Atropisomerism; Combinatorial chemistry; Click chemistry; Azides;*

P-0283

INVESTIGATION OF PHOTO-INDUCED TRANSFORMATIONS INSIDE SOFT GEL MATERIALS: COMPARISON WITH HOMOGENEOUS AND MICELLAR SOLUTIONS

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Supramolecular gels have recently been rediscovered as a new field in supramolecular chemistry and soft matter because they represent a powerful tool to the development of new materials and devices of nanoscale dimensions with tailored functionalities such as high mechanical strength or interesting optical and electronic properties. In general such materials should also be suitable for catalyzing chemical reactions by containing either embedded or covalently bound catalytic moieties. Diffusion-controlled processes within the constrained environment of the dynamic gel medium have gained a lot of interest in scientific research because of their impact on the potential catalytic activity and the control of product selectivities of gel materials. The two key features of gel materials are represented by **a)** the two-phase nature, which allows an easy separation of the catalyst and products and **b**) a much higher accessibility of small reagents to the highly solvated three-dimensional network in comparison to most of the standard heterogeneous catalysts.

In order to investigate the potential application of gels as reaction vessels in catalysis the well studied photo-oxidation of benzylalcohols by flavin derivatives and blue visible light has been chosen as model reaction.

Flavins, which are versatile electron carriers in biological processes have recently gained much attention in chemical catalysis as upon irradiation the redox potential of the flavins increases significantly. Various both biopolymer and low-molecular weight based gel-materials have been applied for the studies.

Structure-property relationships of the different confined environments and their effect on product selectivities and reaction process have been developed by for example oscillatory rheology, electron microscopy, FTIR and UV-spectroscopy, thermal transition temperature and oxygen permeability determinations. It could be shown that several of these materials can efficiently assist the production of desired oxidation products in moderate to excellent yields without byproduct-formation.

Keywords: *Photochemistry; Supramolecular Chemistry; Gels;*

P-0284

ANTHRAQUINONE AS A REDOX LABEL FOR DNA. SYNTHESIS, ENZYMATIC INCORPORATION AND ELECTROCHEMISTRY OF ANTHRAQUINONE-MODIFIED NUCLEOSIDES, NUCLEOTIDES AND DNA

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Electrochemical detection is a less expensive but comparatively sensitive alternative to common optical methods. Particularly efficient is the single-step synthesis of modified dNTPs by cross-coupling reactions followed by polymerase incorporation. We have used this novel approach for the synthesis of DNA bearing a number of redox labels[1], which were successfully used for “multicolor” redox labelling of DNA. Anthraquinones are attractive redox labels suitable for labelling of biomolecules.[2] Our goal was to prepare modified dNTPs bearing anthraquinones attached through an acetylene or propargylcarbamoyl linker to the 5-position of pyrimidine (C) or to the 7-position of 7-deazaadenine and their polymerase incorporation to DNA. Polymerase incorporations of the AQ-labelled dNTPs into DNA by primer extension with KOD XL polymerase have been successfully developed. The electrochemical properties of the AQ-labeled nucleosides, nucleotides, and DNA were studied by cyclic and square-wave voltammetry.[3]

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Keywords: *nucleosides; oligonucleotides; electrochemistry;*

P-0285

RESOLUTION OF TERT-BUTYL-3-HYDROXY-4--PHENYLPYRROLIDINE-1-CARBOXYLATE

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In kinetic resolution two enantiomers react with different rates in a chemical reaction. If there is a large difference between the two reaction rate constants, practically only one of the isomers takes part in the reaction, the other one stays unreacted. Kinetic resolution can be carried out in the presence of chiral catalysts. Enzymes, such as hydrolases are highly suitable for this purpose.[1]

Our goal was to prepare a racemic pyrrolidine derivative and work out its enzymatic resolution. It can be an intermediate of the synthesis of chiral ligands and could be useful for the pharmaceutical industry. Many compounds with the similar structure were proved to have biological effects such as iminosugars, which are potential inhibitors of glucosidase enzymes[2] or kainic acid derivatives that have a potent central nervous system stimulant activity[3].

In the course of our research, we synthesized *trans tert*-butyl-3-hydroxy-4-phenylpyrrolidine-1-carboxylate from *tert*-butyl 6-oxa-3-azabicyclo[3.1.0]hexane-3-carboxylate in a Grignard-reaction. Kinetic resolution of the racemic secondary alcohol was investigated using enzyme catalysed acylation. Series of experiments were accomplished in order to find the most efficient enzyme, solvent and temperature, thus we could prepare the optically active (3*R*,4*S*)-alcohol isomer with high enantiomeric purity.

The optically active ester was separated from the (3*R*,4*S*)-alcohol by flash chromatography. Alcoholysis of the ester was performed in different alcohols catalysed by Novozym 435 enzyme, which proved to be the most efficient in the previous experiments. With this method also the (3*S*,4*R*)-isomer of the alcohol can be prepared in high enantiomeric excess.

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Keywords: *Enzymes; Kinetic resolution; Acylation; Enantioselectivity; Heterocycles;*

P-0286

GROWING POLY(DISULFIDE) CELL-PENETRATING PEPTIDES ON THIOLATED CARGO

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The activities of dynamic polyion-counterion complexes in lipid bilayer membranes have been studied for their scientific utilities as transmembrane transporters / carriers, voltage gates, and sensors. Our dynamic amphiphiles, having dynamic bonds between their charged head and their hydrophobic tails, can activate biomolecules (DNAs, siRNAs, CPPs) as counterion transporters.[1] We currently are expanding this concept to poly(disulfide)s, dynamic polymers with disulfide repeats in their main chain, to deliver biomolecules through the cellular membrane.[2] The disulfide bond is a dynamic covalent bond, which can be easily cleaved and reformed, but stronger than the non-covalent interactions present in supramolecular polymers. Moreover, it is degradable via reductive depolymerization by glutathione in cells. The general objective of this project is to let poly(disulfide) CPPs grow directly on thiolated initiators of free choice (siRNA, drugs, probes) before their cellular uptake, and have them removed afterwards in the cytosol. Here, we report the synthesis of guanidinium-containing disulfide propagators and their polymerization by thiol-initiated ring-opening disulfide exchange.[3] The polymerization and depolymerization processes were monitored by measuring transport activity in fluorogenic vesicles, and by size exclusion chromatography, light scattering and mass spectrometry, including fluorescent initiators and terminators for FRET-analysis. We hope that the resulting method will provide general access to non-toxic delivery in native form.

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Keywords: *Peptides; Polymers; Ring-opening polymerization;*

P-0287

"METAL-FREE" SYNTHESIS OF FUNCTIONALIZED POLYLACTIDE BY CATIONIC ACTIVATED MONOMER POLYMERIZATION

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Poly(lactide) (PLA) is the major bio-based polymer which can be produced from renewable resources. Due to biodegrability and biocompatibility PLA is the candidate of choice for polymeric commodities as well as for application in the medical field.[1]

However a lack of functional group along the polymer backbone considerably limits the possibilities for further chemical modification of polymer chains. To overcome this limitation several approaches has been examined including modification of lactide monomer, copolymerization with suitable comonomer or blending.[2]

Our goal was to develop convenient synthetic procedures for the synthesis of functionalized PLA using "metal-free" catalysts and initiators. Polymers of lactide containing at one or both ends reactive groups that may be used as precursors of segments in block copolymers or side-chains in graft copolymers can be obtained by cationic activated monomer polymerization.[3]

Using functionalized alcohols as initiators we obtained PLA macromonomers carrying unsaturated – (meth)acrylate and propargyl groups at one chain end. One-pot synthesis based on easy available acid and alcohols prevents the possible contamination of the final products with metallic initiators or catalyst residues.

The reactivity of functional groups (containing double or triple bonds) was confirmed by radical (co)polymerization of macromonomers or by performing azide-alkyne "click" reaction with model azide.[4]

PLA containing pendant reactive groups was obtained in cationic copolymerization of lactide with epichlorohydrin. The postpolymerization modification based on these functional polymers may provide entry to expand the application of PLA.

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Keywords: *polymerization;*

P-0288

SYNTHESIS OF TRADITIONAL MEDICINAL FUNGAL METABOLITES.

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In 2009 Proksch *et al.* isolated a number of biologically active fungal metabolites from a *Pestalotiopsis* sp. of fungi, discovered in the medicinal plant *Rhizopora mucronata*, a mangrove found in southern China.[1] The biologically active compounds isolated from the endophytic fungi, may prove to be drug leads which have a history of internal use (non-toxic) and demonstrated activity. Two classes of compounds isolated by Proksch were of particular interest. The pestalotiopsones are a collection of chromone derivatives featuring an alkyl group at C-2 and a carboxyl group at C-5.[1a] Compounds with this substitution pattern are part of a rare subtype of chromones found in nature, with only three previously recorded members.[2] The cytosporones are a group of 3-isochromanones, which are relatively scarce in the natural products literature, possessing an alkyl group at C-2 and varying oxygenation of the aromatic ring.[1b]

The specific rotations of the natural products containing chirality were measured, although the absolute stereochemistry of the compounds was not determined. Synthesis of these compounds is yet to be reported in the literature. This presentation will describe the work leading to the first syntheses of these natural products, and the determination of the absolute stereochemistry of the natural compounds.

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Keywords: *Total synthesis; Natural products; Drug discovery; Heterocycles; Microwave chemistry;*

P-0289

CHOLESTEROL-BORON CLUSTER CONJUGATES: SYNTHESIS VIA DIOXANE RING OPENING OF THE OXONIUM DERIVATIVE OF THE BORON CLUSTER AND PRELIMINARY PHYSICOCHEMICAL AND BIOLOGICAL EVALUATION

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Due to bioorthogonality, lipophilicity or amphiphilicity, rigid, spherical or ellipsoidal shape, chemical stability and resistance to catabolism, carboranes and metallacarboranes are often used in modification of biologically active compounds. The literature comprises numerous examples in which boron clusters are applied as surrogates for heterocycles, annulated carbon rings, or most popularly for substituted or unsubstituted phenyl rings.[1, 2] Among many low molecular weight compounds modified with boron clusters are amino acids, lipids, carbohydrates, porphyrins, nucleic acid bases and nucleosides, and DNA groove binders; boron cluster modified biopolymers include peptides and proteins, nucleic acids (DNA-oligonucleotides) and oligophosphates. Carboranes have been used also in preparation of analogues of biologically active steroids such as estradiol, estrogen receptor modulators or testosterone. [3]

In this communication a general approach to the synthesis of novel type of cholesterol-boron cluster conjugates bearing metallacarborane moiety is described. The method is based on the dioxane ring opening in the oxonium derivative of the boron cluster**.**Possibility of incorporation of the selected conjugates into lipid bilayers and physicochemical and biological characterization of the obtained metallacarborane-incrusted liposomes was also approached.

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Keywords: *carboranes; steroids; liposomes;*

P-0290

N-OXIDE DERIVATIVES OF CHOLESTEROL AND LANOSTEROL

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Pathogenic microbes and fungi represent a significant hazard to multicellular organisms, including humans. In nature, there are substances capable of selectively inhibit the growth of microbes and fungi. Some of these substances contain a peroxide group. We assumed that substances bearing the *N*-oxide group also will have the desired properties. Our goal was to prepare derivatives of phytosterols containing *N*-oxide group for subsequent tests of the biological activity.

Lanosterol and cholesterol were selected as representatives of sterols. For each steroid a series of derivatives was obtained. We obtained four series of derivatives. Each series consisted of derivatives containing the *N*-oxide fragment and derivatives without the*N*-oxide fragment. As a basis containing the *N*-oxide fragment were selected picolylamine derivatives and 2-(4-aminomethylphenyl)pyridine-*N*-oxide. They were obtained in three synthetic stages. Synthesis consisted in protection of the amino group by obtaining FMOC derivative, oxidation by peracetic acid for obtaining *N*-oxide and removing protection group. From the initial steroids hemiesters of succinic acid were obtained. Modified amines bearing *N*-oxide group were coupled with the sterol hemiesters by amide bond. For comparing biological activity, we obtained derivatives of phytosterol hemiesters with picolylamines and 2-(4-aminomethylphenyl)pyridine.

The resulting derivatives were tested for cytotoxicity on the cells of human T-lymphoblastic leukemia, breast adenocarcinoma, cervical cancer, and also on normal human fibroblasts.

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Keywords: *steroids; amines; amides; cytotoxicity;*

P-0291

ADHESION PROPERTIES OF POLYURETHANES PREPARED FROM CIS-1, 4-POLYISOPRENE

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Hydroxyl compounds currently used in the production of polyurethanes (PU) are petrochemical products (polyester and polyether polyols). However, they have some disadvantages as they are non-renewable resources, they may cause environmental pollution, and they tend to be exhausted in the near future. Natural rubber (NR), mainly composed of polyisoprene, is an interesting choice to use as a starting material in PU synthesis, due to the fact that they are renewable source, abundant polymer and they have good mechanical properties and are easy to chemically modify.

Polyisoprene was modified to lead oligomers with reactive terminated groups. The objective of these chemical modifications of polyisoprene is to prepare new polyurethane adhesives using environmentally friendly sources such as NR latex.

The first step of the adhesives preparation is the synthesis of hydroxytelechelic cis-1,4-polyisoprene of various molecular weight. The second step is then the preparation of epoxidized hydroxytelechelic cis-1,4-polyisoprene with different epoxidation levels. Polyurethane adhesives were finally obtained by reaction of hydroxytelechelic oligomers with toluene diisocyanate.

Steel/polyurethane/steel assemblies were obtained after curing of adhesive at 60 °C. A wedge test was used to quantify adherence level of assemblies. A wedge is introduced in the assembly, in air at 20 °C, is then stopped and the crack length is followed until equilibrium. The final crack length was measured for different polyurethanes, prepared from hydroxytelechelic cis-1,4-polyisoprene of various molecular weight and epoxidation degree. Microscopy analysis was used to precisely localize the locus of failure. Surface properties of polyurethane films were also investigated by FTIR spectroscopy (ATR mode) and wettability.

Wedge test results show that some polyurethanes exhibit high adherence level. Adhesive behaviour is discussed as a function of isoprene molecular weight and epoxidation degree.

Keywords: *Polymers; Interfaces; Natural products;*

P-0292

FROM PROPARGYLIC AMIDES TO FUNCTIONALIZED OXAZOLES: DOMINO GOLD CATALYSIS/OXIDATION BY MOLECULAR OXYGEN

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The oxazole nucleus is present in different natural and non-natural compounds possessing biological and pharmaceutical properties. Recently, we have reported the gold-catalyzed cycloisomerization of propargylic amides to alkylideneoxazolines and oxazines.[1] While studying this reaction, it was observed that a different product could be isolated when the reaction mixture was exposed to air. The unexpected product was formed as a result of a spontaneous oxidation mediated by the oxygen present in the air. Such an oxidation is only reported in presence of metals or radical initiators and none of them have been used for the synthesis of oxazoles.

In order to investigate the autoxidation process, different solvents, substrate concentrations and temperatures were tested. It was established that with 0.5 M of the substrate in tetrahydrofuran (THF) at 50°C a faster conversion and higher yields were achieved. Although experiments in absence of oxygen indicated that molecular oxygen is the main oxidizing agent that promotes the conversion, the presence of THF peroxide accelerates the formation of the hydroperoxide. To have a better idea of the possible pathway, some additional experiments were conducted. The oxidation does not take place in presence of the well know butylated hydroxytoluene, and it is accelerated by the radical initiator azobisisobutyronitrile.From these results it is possible to deduce that the oxidation of methyleneoxazolines follows a radical pathway, probably triggered by the combination of high temperature and light and promoted by the presence of oxygen and THF peroxides. The study of the reaction scope proved that the reaction performs with good yields by a wide range of substrates with different electron withdrawing and electron donating groups in the benzene ring, offering a novel access to functionalized 2,5-disubtituted oxazoles with full atom economy.

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Keywords: *Autoxidation; Gold; Oxygen; Peroxides; Cyclization;*

P-0293

SELF-ASSEMBLED TRANSITION METAL COORDINATION POLYHEDRA

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Pyridine based organic ligands have been widely used with transition metals in self-assembly. With this approach different kinds of structures have been reported such as spheres, cubes and tetrahedra.[1-3] In this study different kinds of pyridine ligands were prepared. These ligands have usually two pyridine binding sites with a ligand bend angle varying from 120° to 180°. Depending on the coordination geometry of the transition metals, the bend angle of the ligand and an appropriate stoichiometric ratio of the components can lead self-assembly into specific and discrete three-dimensional assemblies. The ligands have to have a certain amount of rigidity. Too rigid or too flexible ligands may not form discrete structures. Therefore, for achieving a certain defined supramolecular structure the ligand design and the transition metal ion have to be chosen carefully. Preliminary results on the studies of the prepared ligands and their Pd^{2+} and Fe^{2+} ion based assemblies will be presented.

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Keywords: *Self-assembly; Supramolecular chemistry; N ligands; Ligand design;*

P-0294

ESTERIFICATION UNDER MICROWAVE CONDITIONS IN ORGANOPHOSPHORUS CHEMISTRY

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It is known that phosphinic acids cannot be esterified under traditional conditions. Phosphinic esters are usually synthesized by the reaction of the corresponding P-acid chlorides with alcohols and phenols. This method is not environmentally friendly because of the hydrocloric acid liberated. Despite of this it is widely used in the industry. Recent experiments showed that direct esterification of phosphinic acids with primary alcohols under microwave (MW) conditions may be a possible environmentally friendly solution. The fact that the beneficial effects of the MW irradiation causes the novel reaction was proved by comparative thermal experiments.

Our research group has already studied the esterification of phosphinic acids to phosphinates under MW conditions. The direct esterifications using short chain alcohols in 15 times excess were optimized. Applying a reaction temperature of 160–200 °C, the preparative yields were around 45–60%.

Our aim was to study the esterification with branched chain and less volatile (longer carbon chain) alcohols in order to investigate the direct esterification in detail and to synthesize new phosphinates. The new products were characterized by ^{31}P NMR, ^{13}C NMR and ^{1}H NMR, as well as HRMS spectrometry.

Our model compounds were the cyclic hydroxyphospholene- and phospholane oxides, and an acyclic compound, the 1-H-phenyl phosphinic acid.

The novel reaction is promoted by the beneficial MW effect that was proved by comparative thermal experiments.

Keywords: *Phosphorus; Microwave chemistry; Environmental chemistry; Green chemistry;*

P-0295

A SIMPLE NEW METHOD OF THE SYNTHESIS OF METHYL 1,4,5-TRISUBSTITUTED-1H-PYRAZOLE-3-CARBOXYLATES

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A new method for the synthesis of methyl 1,4,5-trisubstitued-1*H*-pyrazole-3-carboxylates which doesn't involve using of hydrazines has been studied. This method can be carried out very simply and under mild conditions. Regarding the complex topic of the synthesis of persubstituted 1*H*-pyrazoles and the importance of pyrazole derivatives as pharmacophores and pesticides, this procedure could be a useful expansion of existing synthetic methods for the preparation of these substances.

Several derivatives have been prepared by means of the basic-catalyzed reaction of "*push-pull*"-polarized *β*-enaminoesters with benzenediazonium-tetrafluoroborates. The reaction mechanism has not been completely described yet, but it probably comprises a double azo-coupling with a subsequent intramolecular cyclization followed by releasing of nitrogen and the corresponding arene. The crucial effect of the basic catalyst has been determined: the reaction does not proceed without its presence and the right choice of the catalyst can affect the regioselectivity of the reaction.

This work follows the recent studies on the synthesis of 3-acyl-4-amino-1-aryl-1*H*-pyrazoles [1–3]. The structures of the prepared products have been verified by means of GC/MS and NMR spectroscopy, some of them also by X-ray diffraction. The reaction conditions and procedures will be further discussed.

Acknowledgement: *The work was supported by Ministry of Education, Youth and Sports (MSM 002 162 7501).*

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Keywords: *Heterocycles; Diazo compounds; Synthetic methods;*

P-0296

TOWARDS THE SYNTHESIS OF SPECIFICALLY 13-C-RING LABELLED PHENYLALANINE

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The development of new isotope labelling strategies for proteins has boosted the development of new methods to study the structure and dynamics of these molecules.

In this study new tools for structural biological problems will be developed. Focus will be set on the preparation of specifically 13-C ring-labeled aromatic amino acids and their precursors, which should be versatile starting points for structural assignments of biopolymers utilizing novel NMR experiments.

The aim of this project is to synthesize specifically 13-C-ring labelled phenylalanine precursors via metathesis reaction. The reaction sequence utilizes the easily accessible protected D-glyceraldehyde, obtained from commercially available D-mannitol, as starting material. The metathesis reaction precursor needed is generated via an indium promoted chain elongation reaction of the aldehyde using α-bromomethacrylate as allyl component. Ring closing metathesis (RCM) yields a cyclohexene derivative which should easily aromatize to benzoic acid. Reduction of the ester moiety to the corresponding aldehyde and further hydantoin elongation should make phenylalanine accessible. The origins of the ^{13}C-labels are the α-bromomethacrylate which has been synthesized in all possible^{13}C-labeling patterns in our group. This route opens the possibility to label exactly defined positions in the aromatic ring. The second optional source of 13-C-labels is the hydantoin, which enables establishing a variety of labelling patterns in the C-3-sidechain of the final amino acids.

Keywords: *Isotopic labeling; Amino acids; Metathesis;*

P-0297

HARNESSING HELICITY FOR ENHANCED FUNCTION

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Helical structures are manifest in nature over many magnitudes of scale from galaxies to biochemistry. Helical structures are chiral yet, arguably underutilised as a design elemnt in asymmetric organic synthesis. This presentation will focus upon our efforts to harness helicity, in the form of helicene-like molecules (helicenoids), examining their efficacy in the context of organocataysis.

Our synthetic efforts to "helical DMAP" and "helical m-CPBA" catalysts will be discussed. Key issues and contexts under discussion in this presentation will be catalyst resolution, point-to-helicity transfer, kinetic resolutions, enantioselective reactions and metal organic frameworks.

Keywords: *Helical structures; Organocatalysis; Synthetic methods;*

P-0298

TANDEM METATHESIS FOR THE TOTAL SYNTHESIS OF LYCORINE TYPE ALKALOIDS

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Our organic synthesis group have developed over the past five years strategies for the synthesis of complex natural alkaloids relying on ring closing metathesis (RCM). This program has led to the efficient asymmetric total synthesis of biologically active natural products such as (+)-castanospermine and (+)-1-deoxynojirimycin, through the development of an original one pot procedure of enol ether RCM – hydroboration that lead exclusively, and in high yield, to a specific *trans-trans* substitution pattern present in numerous alkaloids.

Our attention is now focused on the exploration of tandem ring closing metathesis containing an ynol ether as a partner and its application to the total synthesis of lycorine type alkaloids. The synthesis of the key intermediate for the novel tandem sequence requires the development of two new methods: firstly, the unprecedented addition of alkoxyacetylide to chiral sulfinylimine, and secondly a crucial direct aldolisation of sulfinylimidate. The alkoxyacetylide additions to sulfinylimine proceed with excellent yield and selectivity, and the direct aldolisation is highly promising. These recent results on both fields, allowing a direct access to the key intermediate for the tandem RCM and for the first total synthesis of some lycorine type alkaloids, will be presented.

Keywords: *total synthesis; ynol ether; sulfinylimidate; metathesis;*

P-0299

NOVEL, CLICKABLE FAR RED – NIR MEGA-STOKES FLUOROPHORES FOR BIOORTHOGONAL LABELING, BIOIMAGING AND FRET SYSTEMS

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Chemical labeling of biopolymers are key tools to many applications in biotechnology and medicine. The most convenient and efficient way towards fluorescent labeling of biological targets is bioorthogonal ligation. Among various techniques and reactions, the copper catalyzed azide-alkyne cycloaddition (CuAAC) is the most frequently used one due to the high selectivity and reaction rate of this reaction. Fluorescent labeling is common technique in biological experiments due to its relatively cheap and very sensitive detection. The most-frequently used fluorescent dyes, however, often suffer from drawbacks. Their so-called Stokes-shifts (ea. the difference between the excitation and emission maxima) are only 20-30 nm giving rise to relatively large self-absorption and high background fluorescence, both contributing to lowered detection efficiency. As a possible solution to overcome these limitations, so-called mega-Stokes fluorophores are used with Stokes-shifts larger then 100 nm. The use of fluorescent tags in biological applications often requires emission wavelengths in the far-red – NIR spectral window where the transparency of living cells is the highest and autofluorescence of biological matter is negligible.

With these aims in mind a set of new, azide or alkyne bearing lepidinium-based fluorophores were designed and synthesized for bioorthogonal labeling schemes. These fluorescent dyes all possess large Stokes-shifts with emission maxima in the far-red – NIR regime and can be excited by commonly used laser sources. The *in vivo* applicability and toxicity of these fluorescent dyes were tested in cell labeling experiments with CHO-cells. Furthermore, the applicability of these dyes in the construction of energy transfer (FRET) systems was also tested using one of these new fluorescent tags with daunorubicin, an anticancer drug with fluorescent features. This FRET labeled model system can be used to follow the uptake and the possible release of daunorubicin within cells.

Keywords: *Click chemistry; Fluorescence; Fret; Azides; Alkynes;*

P-0300

NUCLEOSIDE PROBES FOR DETECTING O6-ALKYL-2'-DEOXYGUANOSINE IN DNA

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Alkylation of DNA to form nucleoside adducts is an important transformation leading to mutagenesis and carcinogenesis. A possible means for detecting DNA adducts are hybridization probes, which are oligonucleotides containing nucleoside analogs designed to pair opposite specific adducts, such as O^6-alkyl-2'-deoxyguanosine (O^6-alkyl-dG). Alternatively, polymerase-mediated amplification of adducted DNA to facilitate detection would be desirable. We have evaluated a series of nucleoside analogs for utilization in both hybridization probes and for polymerase-mediated incorporation opposite O^6-alkyl-dG adducts. Results indicate that nucleoside analog size, shape, pi-stacking ability, and hydrogen bonding capacity influence selectivity and effectiveness in hybridization and DNA synthesis.

Keywords: *Alkylation; DNA damage; DNA recognition; Nucleosides; Noncovalent interactions;*

P-0301

HIGHLY ENANTIOSELECTIVE CARBOCYCLIZATIONS BY COMBINATION OF AMINE AND HETEROGENEOUS METAL CATALYSTS

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The first examples of one-pot highly enantioselective dynamic kinetic asymmetric transformations involving α,β-unsaturated aldehydes, propargylated nucleophiles and Pd (II) nanocatalyst. These DYKATs, which proceed by a combination of catalytic iminium activation, enamine activation and Pd (II) nanoparticles supported on aminopropyl-modified siliceous mesocellular foam (MCF) catalyzed carbocyclizations, gives access to functionalized cyclopentanes, dihydrofurans and 2,5 –dihydropyrroles with up to 98% ee. The Pd (II) nanocatalyst was found to be remarkably stable and could be recycled several times with no leaching of the metal into solution or any change in activity.

Keywords: *asymmetric catalysis; organocatalysis; heterogeneous catalysis; palladium; cyclization;*

P-0302

STRUCTURE-PROPERTY RELATIONSHIPS OF LOW-MOLECULAR WEIGHT ORGANOGELATORS BASED ON BIS[N-(P-ARYL)-CARBAMOYLOXY]ALKANES

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The organogelation phenomenon exhibited by low-molecular weight organic compounds is the subject of increasing attention owing to their striking self-assembling properties, their responsive behavior and their applicability.[1, 2] Most organogels immobilizing various organic solvents at relatively small concentrations (≤5% wt) consist of long nanofibers self-assembled through non-covalent interactions. The search for the tuning of mechanical or thermal properties of the gels, the scope of gelated solvents and morphology of the gels is elementary in the field of gel chemistry. It is believed that structural variations provide a basis for a better understanding of the structure-property relationships. With this aim, we synthesized a class of Bis[N-(*p*-aryl)--carbamoyloxy]alkanes and investigated their organogelation properties.

These compounds have been synthesized by the reaction of *p*-aryl isocyanates with diols and their structures have been determined by ^{1}H and ^{13}C NMR. The sol-gel transition temperatures (T_{gel}) were determined by the dropping-ball method and differential scanning calorimeter. The morphology of the organogelators was investigated by scanning electron microscopy.

The compounds were designed on the basis that they have two urethane units capable of forming hydrogen bonds, an aryl moiety substituted by electron-donating groups which increase the strength of p-p stacking and a hydrophobic unit that can be involved in hydrophobic interactions. It has been observed that the synthesized compounds favored the formation of supramolecular gels in alcohols, esters, toluene, xylene, dichloromethane. Infrared spectroscopy indicated that the organogelation occurred through hydrogen bonding. Crosslinked network was observed in the electron micrographs. Different gelation behavior was observed in different solvents by varying the alkyl chain length and the nature of para-substituents. In most of the cases, para-alkoxy derivatives promote gelation at lower gelator concentration compared to para-alkyl substituted compounds.

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Keywords: *Gels; Hydrogen bonds; Supramolecular chemistry; Pi interactions; Self-assembly;*

P-0303

SYNTHESIS OF NEW C-PRENYLATED AND O-PRENYLATED COMPOUNDS: MOLECULES WITH POTENTIAL BIOLOGICAL ACTIVITY

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Magnolol and honokiol, are significant bioactive constituents isolated from the bark of *Magnolia officinalis* which posses potent anti-oxidative, anti-inflammatory and anti-cancer activities [1]. The chemical structure of magnolol is a C_2-symmetry C-C dimer of 4-allyl-phenol which forms a biphenyl skeleton, whereas honokiol is its structural isomer (congener). It is known that the presence of a prenyl or geranyl group in natural polyphenols can lead to a remarkable increase in bioactivity due to an increment of lipophilicity through interaction with cellular membranes.

With the aim to prepare compounds similar to magnolol and honokiol and some polyphenols, commercially available 4,4'--dihydroxy biphenyl, 2,2'-dihydroxy biphenyl, 5,5'-diallyl-2,2'-dihydroxy biphenyl, 4-(4-hydroxy-3-methoxyphenyl)-butan--2-one (zingerone), 4-hydroxy-3-methoxybenzaldehyde (vanillin), 1-(4-hydroxy-3-methoxyphenyl)-ethanone (apocynin), 1-(2-hydroxy-4-methoxyphenyl)-ethanone and 3,4-dimethoxy-benzaldehyde (veratraldehyde) were used as starting materials.

Claisen-Schmidt condensation of aryl aldehyde with the appropriate ketone in the presence of base [2], allowed us to achieve α,β-unsatured ketons and calchones endowed with a free-OH phenolic group in 60-70% yield. Each phenol was treated with three different unsaturated alkyl halogens (allyl bromide, geranyl bromide, 1-bromine-3-methyl butene-2) in acetone, in the presence of K_2CO_3 to give the corresponding *O*-prenylated derivatives in 70-80% yield.

In order to achieve *C*-prenylated phenols, the compounds were further subjected to Claisen rearrangement under both thermal condition and microwave irradiation.

We were able to prepare directly *C*-prenylated biphenol by Heck reaction of linalool with 3,3' dibromo- 4,4'-dihydroxy-1,1'--biphenyl, the latter obtained by bromination of 4,4'-dihydroxy biphenyl in the presence of Br_2 and AcOH.

All synthesized compounds were obtained as air stable solids and easily purified by flash chromatography.

Acknowledgement: *This work has been supported by Sardinia Autonomous Region (L.R., August 7th 2007, n. 7)*

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Keywords: *magnolol; prenylated compund; phenol;*

P-0304

BIFUNCTIONAL MESOPOROUS SILICA NANOPARTICLES VIA CLICK-CHEMISTRY – COOPERATIVE CATALYSIS AT SURFACE

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Mesoporous materials with size-tunable mesopores have been widely used in the past few years. Among these multifunctional catalytic systems have attracted a great deal of interest. Inorganic-organic hybrid-materials like MCM-41 combine both flexibility and ease in synthesis of the organic component as well as rigidity and thermal stability of the inorganic framework.

A precise attachment of organic functionalities onto mesoporous silica nanoparticles (MSNs) can be achieved either by post grafting of an organosilicon compound or by the co-condensation method.

Several examples are known wherein the concept of a dual activation of nucleophiles and electrophiles by acids and bases respectively lead to synergistic catalytic enhancements. Herein we present the synthesis of acid-base bifunctional MSNs via co-condensation of tetraethoxyorthosilicate (TEOS) and various triethoxysilanes bearing orthogonal and therefore subsequently addressable functionalities. Their catalytic performance has been tested in the Henry-reaction.

Via this approach we were also able to bring on ligands at surface and immobilize transitionmetals into the mesoporous particles in order to catalyze cross-coupling reactions.

Keywords: *binfuctional catalysis; mesoporous silica nanoparticles; heterogeneous catalysis; cooperativity;*

P-0305

RUTHENIUM-CATALYZED DIRECT C–H BOND ARYLATIONS OF ARENES BEARING REMOVABLE DIRECTING GROUPS

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Transition-metal-catalyzed direct arylation reactions *via* C–H bond cleavages constitute an economically and ecologically benign alternative to conventional cross-coupling reactions.[1]

In recent years, we have reported on generally applicable, site-selective direct arylations of various arenes using aryl bromides, chlorides, tosylates and phenols as (pre)electrophiles.[2] We disclosed the beneficial effect of carboxylic acids as additives in ruthenium-catalyzed direct arylations [3] or direct alkylations with unactivated alkyl halides.[4] This catalytic system showed a broad scope, and the key C–H bond metalation was proposed to proceed through a carboxylate-assisted mechanism.[3]

However, ruthenium-catalyzed C–H bond arylations of arenes with aryl halides continue to lack generality, as illustrated by their limitation to substrates that form five-membered ruthenacycles.[1–3]

Recently, we devised first ruthenium-catalyzed direct arylations of arenes via six-membered ruthenacycles that set the stage for a removable directing group strategy.[5]

Herein, we present the development, and scope of this transition-metal-catalyzed C–H bond functionalizations.

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Keywords: *C-H activation; Homogeneous catalysis; Ruthenium; Sustainable Chemistry; Arenes;*

P-0306

SYNTHESIS OF A PHOTOSENSITIZER FOR PHOTODYNAMIC THERAPY

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A phenothiazine trimer (N-benzyl-3,7-diphenothiazinyl-phenothiazine) was synthesized for use as a photosensitizer (PS) in photodynamic therapy (PDT). Buchwald-Hartwig chemistry utilizing a Pd catalyst and XPhos ligand resulted in the formation of two new C-N bonds on the benzyl protected phenothiazine base. PDT involves the use of a PS, light, and singlet oxygen to destroy cancer cells. A PS can be administered to a patient, and light of a specific wavelength directed to the cancer site using optical fibers. The light excites the PS and energy is transferred to oxygen to produce singlet oxygen or to nearby molecules to produce radical species. The singlet oxygen and radicals damage vital cellular organelles, and subsequently destroy cancer cells. Highly conjugated photosensitizers will absorb longer wavelengths (600 – 900 nm), and have the potential to destroy cells of deeper tissue tumors.

Future work involves the deprotection of the phenothiazine trimer, and subsequent attachment of a polyethylene glycol (PEG) linker so that the PS is more soluble in aqueous media. The linker will also allow attachment of a folic acid molecule to increase selectivity to cancer cells. Receptor mediated endocytosis will allow preferential uptake of the PS complex into cancer cells. Cross-linked hemoglobin will also be complexed to the PS.

The final phase of the research involves testing the PS complex to assess the killing potential using HeLa and neuroblastoma cell cultures. A colorimetric MTT assay as well as confocal microscopy will be utilized to confirm cell death. The hypothesis is that the cells that have been folate restricted will show the most uptake of PS-folate complex and the greatest amount of cell death.

Keywords: *Cross-coupling; Medicinal chemistry; Palladium; P ligands; Singlet oxygen;*

P-0307

NEW POLYMERIC MATERIALS FROM RECYCLED THERMOSETS

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Polycyanurate ester resins are a relatively new class of high performance polymers developed in the late 1960 as base materials for printed circuit boards. The thermosets obtained via a cyclotrimerization reaction from at least difunctional cyanate monomers, show high glass transition temperatures (up to 400 °C), low dielectric constants, high thermostability, high mechanical strength and good stability against most chemicals. This property-profile makes them useful for fibre-reinforced polymers for applications in the aeronautic field, for outer space and also for the automotive area.

A unique feature of the crosslinked polycyanurate ester resins is, that they can be decomposed easily under defined conditions into small molecules be breaking the chemical bonds, using a class of specific chemical agents. Depending on the particular recycling agent and on the recycling conditions, the composition and the kind of products can be influenced significantly.

The resulting recycling-products, containing - besides other structures - phenoles and triazines can be transformed into new thermosets via simple chemical reactions. The authors obtained bulk and foamed materials from the recycled polycyanurates containing up to 30 mass-% of recycled material. In combination with monomers resp. oligomers from renewable resources, new thermosets with 22 mass-% of recycling- and 22 mass-% of renewable material were synthesized. The new polymers show glass transition temperatures of up to 130°C. Further investigations regarding the characterization of the new recycling-polymers are in progress. For the foamed polymers applicability in the automotive and aeronautic field, e.g. as core materials for sandwich-panels are under test. The non-foamed polymers might be used as impregnation- or coating material.

Keywords: *Polymer; recycling; renewable; thermoset; polycyanurate;*

P-0308

P-CHIROGENIC SECONDARY PHOSPHINE OXIDES: NEW STEREOSELECTIVE SYNTHESIS AND AROMATIC COUPLING OWING TO THE ARYNE CHEMISTRY

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The stereoselective synthesis of chiral organophosphorus compounds interests numerous fields: biological compounds, coordinating chemistry, asymmetric catalyzed reactions by transition metal complexes or organocatalysis.[1]

Among the numerous chiral phosphorus compounds described, the P-chirogenic phosphine derivatives are of particular interest, because the chirality is closed to the metal center.

The stereoselective synthesis of P-chirogenic phosphorus compounds was usually achieved in phosphoryled serie[2] or *via* their borane-complex precursors.[3] In continuation of our work on the stereoselective synthesis of new P-chirogenic building blocks,[3b] we investigated herein the synthesis and the use of secondary phosphine oxides.

We report on one hand, a new stereoselective synthesis of P-chirogenic secondary phosphine oxides, *via* the formation of phosphinous acid borane, previously prepared using the ephedrine methodology.[3b] On the other hand, we also report the use of these compounds for the first stereoselective synthesis of P-chirogenic phosphine oxides bearing an *o*-bromoaryl substituent.[4] The key step of this synthesis is based on the secondary phosphine oxide reaction with an aryne species, *in situ* generated by reaction of 1,2-dibromoarene with the *n*-butyl lithium, then metal-halide exchange.

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Keywords: *P-chiral secondary phosphine oxides; aryne chemistry;*

P-0309

SYNTHESIS AND PRELIMINARY STUDIES OF PORPHYRIN-DOTA LIGANDS AND RELATED HETEROBIMETALLIC COMPLEXES FOR IRM/PET IMAGING.

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Last few years, the multimodal probe concept, that aims to use the same molecule as contrast agent of several imaging facilities, has grown significantly[1]. The project we develop concerns new heterobimetallic complexes for applications to the multimodal imaging field. The scaffold of ligand we propose, consists of two different chelators able to strongly bind metal centers of interest; on one hand a porphyrin derivative, which displays well-known properties, such as fluorescence or metal centers complexation, on the other hand a DOTA derivative, which is already used as Magnetic Resonance Imaging (IRM) contrast agent. One of the main interests of multimodal probes is the same biodistribution of the tracers and the combination of advantages from each technique. The series of ligands that we work on, allow the incorporation of gadolinium(III) into the tetraazamacrocycle cavity, and copper into the porphyrinic cavity[2]. The relaxivity of gadolinium(III) complexes was measured at different fields and temperature. The heterobimetallic complexes obtained are potentially useful for IRM/PET combination, if the radioactive 64Cu is chelated into the porphyrin moiety. Moreover the ligands are designed such as to include an activable function to graft them onto biological vectors[3]

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Keywords: *Porphyrinoids; Heterometallic complexes; Macrocyclic ligands; N ligands; Synthesis design;*

P-0310

[3+2] CYCLOADDITION REACTIONS OF ETHYL (Z)-3- AND METHYL (E)-3-FLUOROPROPENOATE WITH AZOMETHINE IMINE

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Compounds with one or more fluorine atoms have become important in medicinal chemistry, due to fluorine unique electronic properties (the most electronegative atom) and its similar atom radius to hydrogen provides specific properties. The special nature of fluorine imparts a variety of properties in medicine including: enhanced binding interactions, metabolic stability by blocking metabolically sites, and change in physicochemical properties, such as lipophilicity or basicity. Fluorine also improves the molecules lipophilicity which facilitates bioavailability, hence higher benefit at lower dosage.

In the other hand, Pyrazolidine, this is the building block for the compound that we have synthesized, received considerable attention in biological studies, and have been used as antibacterial, antifungal, and ectc. In that respect, there is growing demand for synthetic methods for the preparation of selectivity fluorinated hetrocyclic compounds for use in pharmaceutical and agrochemicals. Introducing of fluorine into 5 membered ring can significantly boosted activity of useful range. Introduction of fluorine into a certain position of a bioactive compound improves the efficiency of medicine by reducing the toxicity of the compound.

The main objective of our research is to synthesis bioactive fluoro heterocyclic systems. Ethyl (*Z*)-3-fluoropropenoate has been prepared in a pure state in 68% yield by a Wittig procedure and methyl (*E*)-3-fluoropropenoate was prepared in 38% yield, and 1- benzylidene-3-oxopyrazolidine-1-ium-2-ide has been prepared in a pure state at 59 % yield.

[3+2] cycloaddition reaction occurs to combine 1-benzylidene-3-oxopyrazolidine-1-ium-2-ide and fluoropropeonate to yield fluorohetrocycles.

Keywords: *Fluorine; Pyrazolidine; [3+2] Cycloaddiotn reaction;*

P-0311

FUNCTIONALIZATION OF POLYMER COATED MAGNETIC NANOBEADS BY MICROWAVE IRRADIATION

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Numerous studies demonstrate that heating by microwave irradiation in sealed vessels can reduce reaction times significantly. Additionally, compared to traditional heating higher product yields are often obtained because of fewer side reactions. The solvent employed plays a decisive role in the effectiveness of the heating by absorbing the microwave irradiation. Many nonpolar solvents, however, absorb little microwave energy. To circumvent this problem strongly absorbing passive heating elements (PHEs) can be added to the reaction mixture, e.g. cylinders made out of silicon carbide.[1] We investigated here if highly magnetic metal nanobeads can act as PHEs. The nanoparticles (Fe/C or Co/C) used in these experiments combine a metal core for rapid microwave absorption and magnetic separation and a shell of carbon for higher stability under basic and acidic conditions, while the high surface area and the good dispersion in the reaction mixture are advantageous in the heat distribution over massive PHEs. Surface functionalization was achieved via radical polymerization leading to a high loading of benzyl chloride moieties (> 3 mmol/g).[2] Starting from these polymer coated nanobeads a recyclable magnetic Wang aldehyde scavenger was prepared by substitution of the benzyl chloride moieties with 4-hydroxybenzaldehyde under microwave irradiation. Similarly, a magnetic borohydride resin was prepared by heating with triethylamine in ethanol and subsequent exchange of the chloride counterion with borohydride. Both substitution reactions proceeded quantitative within minutes under microwave irradiation while conventional heating led to incomplete conversion despite considerably prolonged reaction times (3 days). Building on these results, furan or maleimide moieties could be immobilized as anchors for a thermally triggered and reversible Diels Alder – Retro Diels Alder pathway for the immobilization of fluorescent dyes or even catalysts.

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Keywords: *Nanoparticles; Microwave irradiation;*

P-0312

SYNTHESIS, ANTIOXIDANT AND ANTITUMOR ACTIVITIES OF SOME NEW PYRAZOLOPYRIDINES UNDER MICROWAVE IRRADIATION AND CONVENTIONAL HEATING PART II

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The reaction of DMF-DMA with 1-phenyl-3-(pyridin-3-yl)-1*H*-pyrazol-5-(4*H*)-one (1) gave the corresponding 4-(dimethylaminomethylene)-1-phenyl-3-(pyridin-3-yl)-1*H*-pyrazol-5(4*H*)-one (enaminone) (2). The chemical behavior of (2) with active methylene reagents namely as *β*-ketonitriles, malononitrile, cyanoacetamide, cyanothioacetamide and ethyl nicotinoyl acetate was examined. Also, the reaction of (**2**) with some 3-substituted-5-amino-1*H*-pyrazoles was prepared to give bis-pyrazolopyrimidine derivatives. All the prepared compounds were carried out by conventional heating and microwave irradiation technique to give the same products. The results of both methods were compared including yield and time of the reactions. The antioxidant activity of the prepared compounds was studied. Also, some of the prepared compounds were tested for antitumor activity against liver and breast cell lines.

P-0313

COMPUTER-AIDED DESIGN, SYNTHESIS, AND BIOLOGICAL EVALUATION OF NOVEL 2-SUBSTITUTED AMINOMETHYLENEPYRIMIDINE--2,4,6-TRIONES AS H1 ANTIHISTAMINIC AGENTS (PART 2)

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As a part of a research project pertaining to the synthesis of novel candidates as nonsedating, nonclassic histaminergic (H_1) blockers with low toxicity profiles, some new 2-substituted aminomethylenepyrimidine-2,4,6-triones were designed based on the H_1histaminic receptor pharmacophore model. The interactions between the designed compounds and the H_1 receptor were studied using molecular docking on the homology model of H_1 receptor. The designed compounds were synthesized and biologically evaluated for H_1-blocking activity; using isolated segments from guinea pig ileum. Some compounds exhibited comparable activities to acrivastine as reference nonsedating drug. The C log P of designed compounds revealed lower values in relevance to acrivastine which might indicate decreased tendency for crossing the blood brain barrier.

Keywords: *histaminic receptor; pharmacophore model; histaminergic blockers;*

P-0314

SELECTIVE ARENE FUNCTIONALIZATION THROUGH SEQUENTIAL OXIDATIVE AND NON-OXIDATIVE HECK REACTIONS

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The oxidative Heck reaction, so-called *Fujiwara-Moritani* reaction, is an environmentally and economically attractive process for C-C bond formation between olefins and arenes. Compared to the classical *Mizoroki* Heck reaction there is no necessity for prehalogenation of the substrate. The bond formation is realized by an oxidative Pd-catalyzed cross-coupling reaction via direct C-H-activation.[1]

This type of reaction allows regioselective functionalizations of arenes in the presence of electron donating and catalyst directing groups e.g. the acetamide group. The Lewis-basic character of the acetamide group facilitates the coordination to the transition-metal catalyst, which enables an intramolecular insertion of palladium into the C-H-bond selectively in *ortho*-position to the directing group.[2]

Furthermore the acetamide group can be used in the previously investigated deacetylation-diazotation sequence: an operationally simple one-flask procedure which leads to isolable diazonium salts. Arene diazonium salts in turn are powerful reagents for Pd- catalyzed coupling and cross-coupling reactions.[3] Via a non-oxidative Heck reaction traceless removal of the acetamide and regioselective synthesis is achieved simultaneously. The described properties of the acetamide group open up an opportunity to combine oxidative and non-oxidative Heck reactions.

The dual exploitation of the acetamide group as an arene activating and catalyst directing group in oxidative Heck reactions as well as a leaving group in a deacetylation/diazotation/ Heck coupling enables a regioselective synthesis of dialkenylated arenes from acetanilides.[4]

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Keywords: *C-H activation; Heck reaction; Palladium; Diazo compounds;*

P-0315

OLIGOTHIOPHENES WITH NAPHTHALENE BRIDGING MOIETY: RELATIONSHIP BETWEEN STRUCTURE AND SEMICONDUCTING PROPERTIES

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Organic semiconducting materials offer an attractive alternative to conventional inorganic technology because they require less complex fabrication processes[1]. π-Conjugated organic semiconductors are, therefore, attracting considerable attention for application such as organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs), and photovoltaic cells. Their properties can be easily tuned by modification of the structure.

Novel oligothiophenes were prepared via microwave assisted Suzuki cross-coupling reaction between hexylbithienylboronate and corresponding dihalonaphthalenes. Electrochemical properties of each derivative were characterized. OFET-s, prepared by tilt-casting on Si-substrates, exhibit thin film mobilities up to $3.6 \times 10^{-2} cm^2 V^{-1} s^{-1}$. Comparison of the functional properties and their relationship to the molecular structure of prepared derivatives will be presented.

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Keywords: *oligothiophene; organic semiconductors; mobility; organic field-effect transistor;*

P-0316

BRIDGE-MODIFIED CALIX[4]ARENES AS POTENT HOST COMPOUNDS WITH CHEMOSENSING FEATURES

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Calixarenes demonstrate one of the most famous supramolecular hosts, available for inclusion of ionic and neutral guests as well as larger biomolecules depending on chemical modification. Besides the synthetical adaptation of the longitudinal axis of the chalice various approaches have been presented during the last two decades including the modification of the methylene bridge of calix[4]arenes. This horizontal expansion seems beneficial both for the direct incorporation of chemosensing units as well as anchoring of the calixarenes by means of the attachment of sticky- or spacer groups.[1–3] Synthetical attempts and sensing properties of novel bridge functionalized calixarenes are presented.

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Keywords: *calixarene; supramolecular chemistry; lateral substitution; fluorescence sensor; molecular recognition;*

P-0317

SYNTHESIS AND ANTIPROLIFERATIVE ACTIVITY OF NEW IODINE GONIOFUFURONE ANALOGUES

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Goniofufurone is a naturally occurring styryl lactone that exhibits a potent antitumour activity. Herein we want to report preparation of novel goniofufurone analogues (**4** and **5**) having an iodo-deoxy function at the C-7 position and a lipophylic 5-O-benzyl function. 3-*O*-benzyl-1,2-*O*-isopropylidene-5-*C*--phenyl-α-d-*gluco*-pentofuranose (**1**) that was readily available from d-glucose in four steps was conveniently used as a starting material in this work. Hydrolytic removal of isopropylidene protective group in **1**gave the expected lactol **2**, which was converted to the lactone **3** after treatment with Meldrum's acid. Finally, direct substitution of benzylic alcohol function in lactone **3** with iodo isostere was achieved under the Garegg-Samuelsson conditions. The synthesized analogues were evaluated for their *in vitro* cytotoxicity against several human tumour cell lines, as well as normal foetal lung fibroblasts (MRC-5). The preliminary results of their antiproliferative activity will be presented and discussed.

Keywords: *Antitumor agents; Medicinal chemistry; Synthetic methods;*

P-0318

TADDOL-DERIVED PHASE-TRANSFER CATALYSTS FOR THE ASYMMETRIC A-ALKYLATION OF GLYCINE SCHIFF BASES

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Recently, the range of reactions that can be catalysed by phase-transfer catalysts (PTCs) has increased significantly. Besides privileged catalysts[1], like Maruoka's C_2-symmetric BINOL-derived PTCs and cinchona PTCs, no other such powerful compounds have been reported. Although, tartaric acid is one of the most important chiral natural substances, it's use in asymmetric phase-transfer catalysis has to our knowledge been limited to a few examples only.[2]

With the before mentioned structures in mind and as both tartaric acid enantiomers are easily available, we envisioned the design of novel TADDOL[3]-derived chiral spiro ammonium salts as potent compounds for asymmetric reactions.[4]

An overview of our research group's investigations to successfully synthesize a series of new PTCs and to identify the most potent key-structural motives will be given. Ongoing structure modifications and their influence on the catalytic potential for the stereoselective α-alkylation of glycine Schiff bases will be reported.

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Keywords: *Asymmetric catalysis; phase-transfer catalysis; organocatalysis; alkylation; amino acids;*

P-0319

SS-CYCLODEXTRIN BASED DUPLEXES CONNECTED WITH TWO DISULFIDE BRIDGES: SYNTHESIS, STRUCTURE AND INCLUSION COMPLEXES

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Cyclodextrins (CD) attract attention of researchers from different fields because of their unique hydrophobic cavities which can host a range of organic compounds in aqueous media. Various derivatives of CDs were synthesized to improve their binding affinity. In our group, we are interested in the development of a new type of rigid tubular receptors composed of two CD macrocycles connected with two or three flexible disulfide bonds[1, 2].

Recently we have prepared a new β-cyclodextrin duplex and studied its binding properties. The synthesis of the new host compound consisting of two β-CD macrocycles connected with two disulfide bonds in a "head to head" manner was achieved in six steps starting from perbezylated β-CD. In the last oxidation step the predominance of formation of two isomers of the dimer can be attained under conditions of thermodynamic control. Binding affinities to various guests, including clinically used drugs, in the range $Ka = 10^5\text{-}10^8\ M^{-1}$ was determined by isothermal titration calorimetry, demonstrating thus a great potential of ββ-duplexes as a new host system, which could find a broad application in medicine and other areas of research.

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Keywords: *Cyclodextrins; Water chemistry; Host-guest systems;*

P-0320

TOTAL SYNTHESES AND BIOLOGICAL EVALUATION OF NOVEL FLAVONOID DERIVATIVES AS POTENTIAL COX-2 INHIBITORS

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Cyclooxygenase-2 (COX-2) catalyses the production of prostaglandin E2 which is a key mediator of pain and inflammation[1, 2]. Thus, COX-2 enzyme is the molecular target for the therapeutic effect of non steroidal anti-inflammatory drugs[3].

In addition, numerous reports demonstrate that flavonoids, a wide family of natural compounds, inhibit COX-2 activity[4].

We are interested in the pharmacomodulation of flavonoids in order to develop novel COX-2 inhibitors. Therefore, pharmacophores associated with COX-2 inhibition and other functional groups, that seem to improve the expected biological activity, have been introduced on the flavonoid skeleton.

2'-hydroxychalcones were synthesized through Claisen-Schmidt condensation between an acetophenone and a benzaldehyde both bearing a pharmacologically active substituent[5]. These chalcones are key compounds from which other flavonoids, such as flavanones, flavones and flavonols, were obtained.

The synthetic methodologies and the biological results of these molecules will be presented.

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P-0321

CHLOROSTYRENES IN IRON-CATALYZED CROSS-COUPLING REACTIONS

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Metal-catalyzed cross-coupling reactions have matured to an indispensable tool for the functionalization of aromatic molecules. While the majority of protocols utilize electrophilic aryl bromides and aryl iodides, reactions with economically more attractive aryl chlorides remain a challenge for which only a handful of catalyst system exhibit satisfactory activity.[1] We wish to report on our efforts to design a cross-coupling reaction that takes advantage of the activation of aryl chlorides by vinyl substituents. Highly chemoselective iron-catalyzed cross-coupling has been observed under conditions commonly unsuitable for the consumption of deactivated aryl chlorides.[2] The mechanism is believed to involve initial coordination of the vinyl group to the iron catalyst, haptotropic migration along the conjugated p-system to the site of C-Cl bond cleavage.[3]

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Keywords: *Iron-Catalysis; Biaryls; Aryl-Chlorides; Substituted Styrenes; Cross-Coupling;*

P-0322

NEW PHOSPHOROUS LIGANDS DERIVED FROM BENZOXANTHENES

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Aryl-14H-dibenzo[aj]xanthene derivatives have significant biological activities as antibacterials, antivirals, anti inflammatory agents in photodinamic therapy. Xanthene-based compounds have also been investigated for agricultural bactericide activity and some other benzoxanthenes also used in industries such as dyes in laser technology and fluorescent materials for visualization of biomolecules.[1] Moreover, interesting scaffold of dibenzoxanthene structure bring its' possible catalytic activity to mind according to have resemblance to chiral phosphine ligands. These ligands have common applications in enantioselective organic reactions reactions.[2] In the present study, because of potentitial catalytic activity, effective synthesis of dibenzoxanthene compounds containing phosphorous ester moiety and analysing their catalytic activity have aimed.

The synthesis of dibenzoxanthenes by the reaction of aldehydes with 2-naphthol in the presence of various acid catalyst is the most convenient method. In the present study, In order to prepare phosphorus ligand of benzoxanthenes, hydroxyaldehydes and dihydroxynaphthols were reacted in presence of different catalyst, i.e strongly acid catalyst Amberlyst-15, or P_2O_5.[3] Then, phosphoros ester of dibenzoxanthene derivatives synthesized by the reaction of dichlorophenyl phosphine oxide and dibenzoxanthene derivatives.

In the next step phosphine oxide containing dibenzoxanthene compounds will be attempted in organic reactions and their enantioselectivity will be examined.

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Keywords: *Benzoxanthene; Phosphorous ligands; Catalyst;*

P-0323

AMBERLYST-15 CATALYZED SYNTHESIS AND REARRANGEMENT REACTIONS OF 2-TETRAHYDROFURANYL ETHERS

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The conversion to tetrahydropyranyl (THP) or tetrahydrofuranyl (THF) ethers are a part of an important method for protecting alcohol functional groups. It is well known that, in comparison with THP ethers, THF ethers have the advantage that they can be hydrolyzed under even milder acidic conditions and also they can be selectively cleaved in the presence of THP ethers.[1]

There are mainly two methods for the preparation of tetrahydrofuranyl ethers; the first one is using 2,3-dihydrofuran (DHF) in the presence of various acid catalysts, including $Al(OTf)_3$[1], or pyridinium p-toluenesulfonate (PPTS)[2]. The second is based on the use of tetrahydrofuran, THF, in the presence of one-electron oxidants like $CrCl_2$-CCl_4[3] etc. progressing in radicalic pathway.

In our study, a simple and one step method for the conversion of naphthols and phenols into corresponding 2-aryltetrahydrofurans using Amberlyst-15 in THF is reported. This is the first example of the acid mediated formation and rearrangement reactions of tetrahydrofuranyl ether prepared from tetrahydrofuran and aromatic hydroxyl compounds. Corresponding THF ether of 2-naphthol was formed in 3% yield but it was accompanied by the rearrangement product in the yield of 40 %. Treatment of various aromatic compounds which have a free OH group gave *o*-substituted rearrangement products accompanied by a small amount of tetrahydrofuranyl ethers. Reaction can proceed in two steps: In the first step,THF was oxidized to 4-hydroxybutyraldehyde and it reacted with 2-naphthol to form tetrahydrofuranyl ether, then in the presence of strong acid catalyst, Amberlyst-15, Fries rearrangement reaction occurred.

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Keywords: *2-aryltetrahydrofurans; tetrahydrofuranyl ethers; Amberlyst-15; rearrangement reactions;*

P-0324

NEW TANDEM METATHESIS-ISOMERIZATION SEQUENCES AND THEIR APPLICATION FOR NATURAL PRODUCT SYNTHESIS

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During the last decade the ruthenium-catalyzed metathesis reaction was established as an important C-C-bond formation in organic synthesis.[1] Especially the development of tandem metathesis reactions has attracted a lot of attention, e.g. the metathesis-isomerization[2] sequence. Thereby, after completion of the metathesis step the metathesis-active ruthenium carbene species is converted in situ to an isomerization-active ruthenium hydride species by adding an additive.

We developed two new tandem metathesis-isomerization sequences:[3] cross metathesis-isomerization/tautomerization of allylic alcohols and the ring-closing metathesis-isomerization of protected nitrogen precursor to isomerized tetrahydropyridine. Cross metathesis of allylic alcohol is performed with either acrylate or styrene to obtain the enol as an intermediate, which tautomerizes to 1,4-dicarbonyl compound or dihydrochalcone, a class of natural products. The *N*-ring-closing metathesis-isomerization allows a new access of imino sugars.

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Keywords: *Homogeneous catalysis; Ruthenium; Metathesis; Isomerization; Azasugars;*

P-0325

INSIGHTS INTO ASYMMETRIC ORGANOAUTOCATALYTIC MANNICH REACTIONS

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Asymmetric autocatalytic reactions are among the most fascinating processes in catalysis. Several examples are known, the most prominent of which is the Soai reaction for its ability to amplify a tiny initial enantiomeric excess of a chiral pyrimidyl alkanol in the presence of *i*-Pr_2Zn to almost enantiomeric purity.

In 2007, the Tsogoeva group demonstrated for the first time that even in quite ordinary and reversible asymmetric and fully organic reactions, the chiral product alone could act as a catalyst with high stereoselectivity. Realising further that chiral autocatalysis is key to spontaneous mirror symmetry breaking, we have demonstrated for the first time that spontaneous random generation of enantiomeric excess is possible in common asymmetric and fully organic reactions - the aldol and Mannich reactions, even if they are run under essentially achiral conditions and in a system closed to matter flow.

Very recently we have gained further insights on the Mannich reaction, carried out without external catalyst, reconfirming our earlier observations, while the mechanism to explain the emergent product enantiomeric excesses observed could still not be elucidated. Based on ESI-MS measurements and time-resolved ^{1}H-NMR studies we proposed the *in situ* formation of several side products, which could assist in enolate formation from the ketone, and, hence, promote the reaction. Our most recent results on reaction kinetics of this transformation using ^{1}H NMR studies, which are evidence of an induction period of product formation, indicating involvement of an autoinductive or autocatalytic process, will also be discussed in this presentation.

Keywords: *Autocatalysis; Organocatalysis; Kinetics; Mannich bases; Reaction mechanisms;*

P-0326

SYNTHESIS OF CYCLOPROPANES VIA PHASE-TRANSFER CATALYSIS

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Three-membered ring systems like epoxides, aziridines, and cyclopropanes have attracted considerable interest in the scientific community over a long time. Their syntheses are usually either achieved starting from olefins or carbonyl compounds, respectively imines. Surprisingly, the phase-transfer catalyzed synthesis of (chiral) cyclopropanes has so far been described only occasionally, thus leaving space for further improvements.[1]

Combining our recent research interests into the synthesis of three-membered ring systems [2] and the development of new chiral phase-transfer catalysts [3] we have started investigations concerning the synthesis of chiral cyclopropanes by reacting α-halo carbonyl nucleophiles with Michael acceptors in the presence of chiral phase-transfer catalysts.

Initial attempts show promising results. A detailed discussion will be provided on the poster.

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Keywords: *Phase-transfer catalysis; Asymmetric synthesis; Chirality; Michael addition; Cyclization;*

P-0327

SYNTHESIS OF RUSCOZEPINE A AND B, NOVEL NATURAL PRODUCTS ISOLATED FROM BUTCHER'S BROOM

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The novel natural products, Ruscozepine A and B, have been isolated from *Ruscus aculeatus* L., also called Butcher's Broom.[1] An extract from the roots of this shrub is already used for the treatment of various diseases, including chronic venous insufficiency [2] and hemorrhoids.[3] The pharmacological activity is mostly ascribed to the steroidal saponins and ruscinogens, being the main constituents of the Rusci rhizoma extract. However, nothing is known about the influence on the pharmacological effects of the novel found Benzoxepines. Because of the low availability of these compounds by isolation, a synthetic approach was needed to guarantee the supply for extensive pharmacological testing. Beside the synthesis of the isolated compounds a few analogues substances, e. g. Benzazepines, are synthesized to create a small substance library.

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Keywords: *Natural products; Enantioselectivity; Biological activity; Synthetic methods;*

P-0328

CONTROLLED SYNTHESIS OF SMART DRUG DELIVERY SYSTEM FROM VEGETABLE OIL

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Since liposomes were first described in the 1960s and proposed as carriers of proteins and drugs for disease treatment, they have been extensively studied and their efficiency as drug delivery systems has been demonstrated.[1] However liposomology still faces major deficiencies, partly due to their large size.[2] Developing new vectorisation systems of smaller size, typically micelles, but having the same affinity with cells membrane is then of great interest and our group is consequently interested in synthesis of amphiphilic block copolymers containing a hydrophobic block based on a lipid chain. In that purpose, an original synthetic pathway in two main steps was chosen: (**1**) the vegetable oil is first chemically modified to introduce an initiating site for Atom Transfer Radical Polymerization (ATRP) leading to a lipoinitiator and (**2**) a synthetic hydrophilic block is added to the lipid block using ATRP.

The final amphiphilic copolymers are soluble in water, leading to uncolored and foaming solutions. The properties and structure of this innovating micellar system are studied. The micelles present low critical micelle concentrations with a strong dependence to the pH value and a linear dependence to the hydrophilic block length. The micelles ability to encapsulate hydrophobic molecules has been demonstrated and their release properties are currently under investigation as well the polymerization of other monomers to access "intelligent" systems.

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Keywords: *Drug delivery; amphiphiles; lipid; renewable resources; Polymers;*

P-0329

TOWARDS A LIGHT DRIVEN PROTON PUMP

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Light driven uphill transport of protons is an essential process in nature. In the photosynthetic apparatus, light energy is used to pump protons across a cell membrane.

In our model system, the proton transfer is realized by a photo-switchable acid, such as 2-(2,4-dinitrobenzyl)pyridine (DNBP), attached to a [2]rotaxane. Upon irradiation, the photo-switchable acid tautomerizes to a more acidic form and protonates the macrocycle. Due to electrostatic repulsion with a permanent positive charge on the axle, the macrocycle moves along the axle. After the release of the proton, the macrocycle returns to the starting position.

For the realization of this model system, several novel DNBP derivatives were successfully synthesized including the development of a new method to obtain di- and trinitrobenzyl substituted pyridine derivatives.[1] Furthermore, several axles and macrocycles[2]were synthesized and assembled to yield a [2]rotaxane.

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Keywords: *Supramolecular chemistry; Rotaxanes; Proton transport;*

P-0330

SYNTHESIS AND CHARACTERISATION OF PROVED AND POTENTIAL METABOLITES OF MEPHEDRONE

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In recent years, a new class of designer drugs has appeared on the drug of abuse market in many countries. Global increase in the abuse of 4'-methylmethcathinone (mephedrone) and related compounds created a requirement for full chemical characterisation of these products and their metabolites.[1, 2] In this work we present full synthetic and chemical characterisation data for proved and potential metabolites of mephedrone.

Starting from 1-(*p*-tolyl)propan-1-one [3,4] several mephedrone derivatives, mainly, 1-(4-(hydroxymethyl)phenyl)-2-(methylamino)propan-1-one, 2-amino-1-(*p*-tolyl)propan-1-one, 2-amino-1-(4-(hydroxymethyl)phenyl)propan-1-one, 2-amino-1-(*p*-tolyl)propan-1-ol, 4-(1-hydroxy-2-(methylamino)propyl)benzoic acid and some others were prepared by step-by-step syntheses. All the above mentioned mephedrone metabolites were synthesised as hydrochloride salts and will be used as synthetic standards for metabolism studies. Reaction conditions as well as various possible synthetic approaches to mephedrone metabolites will be discussed.

Acknowledgement: *Financial support by grant VG2VS/200 from the Ministry of Interior of the Czech Republic is gratefully acknowledged.*

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Keywords: *mephedrone; metabolism;*

P-0331

MUTINUCLEAR NMR STUDIES OF POLYGLUTAMIC ACID COMPLEXES WITH METAL IONS

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The structures of poly(α-D-glutamic acid)(PGA) complexes with mono-, di- and tri-valent metal ions in solid state were characterized with multinuclear(^{1}H, ^{13}C, ^{23}Na, ^{25}Mg, ^{27}Al) NMR spectroscopy. Most of PGA complexes with di- and tri-valent metal ions take an α-helical conformation as judged from the chemical shift values of the main-chain carbon resonances in ^{13}C CPMAS NMR spectra, while PGA-Na shows the disordered state. Their helical content of the complexes, which were estimated from the line shapes of their resonances, was found to remarkably depend on their ionic radius used. The chemical shift value of the carboxylate carbon in the side chain participated in the complex depends on the ionic radius as well, suggesting the diversity of the distance between the carboxylate and the metal ion.

^{13}C-^{1}H HETCOR NMR spectra were obtained to ensure the spatial information of the complexes through ^{1}H spin-diffusion. The direct C-H correlation signals of the complex were observed for a short CP time, and further two- and three-bonds correlation signals were observed as well for longer CP time. The two bond correlation signal between NH and Cα in the main chain was observed at CP of 100us for helical complexes, while it was observed at longer CP of 500us for disordered PGA-Na, showing the structural difference between ordered(helical) and disordered conformation of polymers.

A single and almost symmetrical resonance with the half width of 3.4 kHz was observed at -13.1 ppm in ^{25}Mg MAS NMR spectrum for PGA-Mg. The main signal of the isotropic chemical shift of -3.8ppm and the quadrupole product of 1.6 MHz was appeared in ^{25}Mg 3Q MAS NMR spectrum, as well as the minor signal of -0.2 ppm and 2.8 MHz, showing two distinct Mg bindings. Other results will be presented in the poster.

Keywords: *polyglutamic acid; metal complex; NMR;*

P-0332

SYNTHESIS OF P-NITROPHENYL SS-D-GLYCOSIDES OF DISACCHARIDE OF HOMOXYLAN TYPE AND TRISACCHARIDE OF 4-O-METHYL-GLUCURONOXYLAN TYPE

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Synthesis of oligosaccharides related to hemicelluloses of xylan type has been developed mainly for characterization of the structural features, physicochemical and various functional properties of these natural polysaccharides.

This contribution describes the synthesis of two model di- and trisaccharides of xylan type, namely *p*-nitrophenyl 4-*O*-(2-*O*-benzyl-*β*-D-xylopyranosyl)-*β*-D-xylopyranoside (1) and *p*-nitrophenyl 4-*O*-[2-*O*-(methyl 4-*O*-methyl-α-D-glucopyranosyluronate)-*β*-D-xylo-pyranosyl]-*β*-D-xylopyranoside (2) in order to serve as the chromogenetic substrates for testing of xylanase belongs to the GH5 family.

The starting point in the synthesis of disaccharide 1 was nucleophile *p*-nitrophenyl 2,3-di-*O*-benzoyl-*β*-D-xylopyranoside[1] which was coupled with 3,4-di-*O*-acetyl-2-*O*-benzyl-*α*,*β*-D-xylopyranosyl acetimidate (prepared from 1,3,4-tri-*O*-acetyl-2-*O*-benzyl-D-xylopyranose[2]). The final disaccharide 1 was obtained by deacylation of the isolated blocked disaccharide from the reaction mixture in a good yield. For preparation of model trisaccharide 2, related to 4-*O*-methylglucuronoxylan, the 3,4-di-*O*-acetyl-2-*O*-(methyl 2,3-di-*O*-acetyl-4-*O*-methyl-*α*-D-glucopyranosyluronate)-*α*,*β*-D-xylopyranosyl acetimidate[3] was used as a glycosylating agent in a coupling reaction with *p*-nitrophenyl 2,3-di-*O*-benzoyl-*β*-D-xylopyranoside. The protected trisaccharide isolated by chromatography after deacylation gave aimed 2 in a satisfactory yield. The structure of both model oligosaccharides 1 and 2 and also their precursors was confirmed by NMR spectroscopy.

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Keywords: *oligosaccharides; synthesis; p-nitrophenyl glycoside; chromogenetic substrate;*

P-0333

COMBINATORIAL SYNTHESIS, SCREENING AND PHOTODEGRADATION OF PHOSPHORESCENT METAL COMPLEXES FOR OLEDS.

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While there have been thousands of reported transition metal complexes for OLED applications in the last decade, an accurate prediction of their photophysical properties and especially their device stabilities/degradation mechanisms is not yet feasible. Therefore the laborious synthesis, purification characterization and testing of a larger number of compounds is still inevitable for the development of new phosphorescent emitters with improved performances.

We report the combinatorial synthesis and screening of phosphorescent iridium complexes as solution processable emitters for OLEDs. Our approach allows for the rapid library synthesis, as well as the isolation, spectroscopic characterization and identification of the compounds based on chromatographic methods. Subsequent analysis of the irradiation induced degradation provides insight on the stability of the complexes under continuous excitation. Utilizing the developed screening methodology we purified and characterized a larger number of potential emitters. We examined the photophysical properties of the compounds by obtaining absorption and emission spectra directly from the chromatographic separation. Important trends in the dual emission behavior of selected heteroleptic complexes were observed that upon further studies might lead to the development of promising new compounds for white OLEDs. By investigating the photodegradation of the libraries in solution, we found surprising trends and could identify compounds with increased stabilities compared to the rest of the libraries. Further studies into degradation mechanisms and to elucidate possible connections between the device- and photo-stabilities are in progress. The gained insight into degradation mechanisms and structure property relationships will help in the design of phosphorescent dopants with improved performances. The reported chromatography based screening of organo-transition metal complexes is by no means restricted to the development of new OLED emitters but may be easily applied for the accelerated discovery of other metal complexes or organic dyes for various applications, e.g. in electroluminescence, photovoltaics and sensing.

Keywords: *Phosphorescence; combinatorial synthesis; Iridium Complexes; Screening; Oled;*

P-0334

Photoswitchable Monolayers: A Dynamic Control over Cell Adhesion

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Photoswitchable monolayers of azobenzene derivatives mounted on glass, quartz or silicon surfaces offer an effective control over cell adhesion. The light induced reversible *cis-*/*trans*-isomerization of azobenzenes permits a precise temporal and spatial control of surface properties.

We employed three strategies:

1. Switching of wettability

Upon isomerization of the azobenzene derivative, the surface wettability changes due to different dipole moments of the azobenzene isomers. This is especially the case when using polar head groups.

2. Fast oscillations

Upon irradiation with white light, azobenzenes with push/pull substitution patterns are known to undergo a fast continuous switching between their *cis-* and *trans*-isomers.[1] We intend to utilize this effect to create a fast oscillating monolayer on surfaces.

3. Integrin mediated adhesion

The establishment of an arginine-glycine-aspartate (RGD) tripeptide squence cell binding domain on surfaces offers the opportunity to target specific integrins of cells. We have chosen the c(-RGDfK-) peptide[2] as our future head group for this purpose, due to its specific binding to $\alpha_v\beta_3$ integrin.

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Keywords: *Cell Adhesion; azobenzene; monolayers on glass; photoswitchable monolayers;*

P-0335

SYNTHESIS OF TRI- AND TETRASUBSTITUATED BENZENE DERIVATIVES ORGANOCATALYTICALLY

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Organocatalysis is a new, environmentally friendly synthetic approach in organic chemistry. In this method, small organic molecules are utilized to realize selective reactions. A frequent application is the use of different organic basis in Michael-type additions.

Recently, we have initiated a program to tandem reaction between appropriate dielectrophiles and dinucleophiles to synthesize even highly substituated aromatic molecules, which difficult to obtain.

Therefore the dimethylglutaconate, as a dinucleophile, was reacted with different α,β-unsaturated aldehydes and ketons. The first step is a Michael-addition, subsequently followed by a condensation. The formed cyclohexadienes could be easily oxidized to the desired benzene derivatives.

We have examined whether this synthesis route is possible without any transition metal, from simple and cheap starting materials using also easily prepared, cost effective catalysts under mild conditions.

We would like to present on the poster the development of the organocatalytic process, the optimalization of the conditions and some possible applications.

Keywords: *organocatalysis; Michael addition; cyclization; oxidation;*

P-0336

SYNTHESIS AND BIOLOGICAL EVALUATION OF FERROCENYL-IMONUSUGARS AS FUCOSIDASE INHIBITORS FOR ANTICANCER THERAPY

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Glycosylation affects many properties of glycoproteins, including their conformation, flexibility and hydrophobicity. As a result, it regulates proteins sorting, stability and protein-host interactions. Fucosylation of glycoconjugates in mammalian organisms is related to a variety of biological processes including cell adhesion, blood antigens and severe diseases like cancer metastasis.[1] Fucosylation of glycoproteins is mainly assumed by two classes of enzymes, fucosidases and fucosyltransferases, the activities of which are markedly enhanced in several types of cancer cell lines.[2]

New drugs aimed at controlling the processing of fucose (fucosidase inhibitors) could selectively target abnormal cells. Moreover, the structural combination with a covalently linked cytotoxic moiety (ie ferrocene) could induce a strong antitumoral activity.[3] Iminosugars (nitrogen-containing sugar analogues) are potent inhibitors of fucosidase with Ki's in the nM range.[4] These alkaloids compare favourably with the natural substrate of enzyme in terms of conformation and hydroxyl distribution. Thus, we targeted unprecedented ferrocenyl-iminosugars as first models for our study. The synthesis, the biologic results and the structure / activity relationships of a series of such compounds will be presented.

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Keywords: *cancer; inhibitors; carbohydrate;*

P-0337

ACTIVATION OF A CARBON-BROMINE BOND BY HALOGEN-BOND DONORS

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Halogen bonds are attractive non-covalent interactions between terminal halogen atoms in compounds of type R-X (X = Cl, Br, I) and Lewis bases.[1] Strong halogen bonds are only obtained for very electronegative rests R. The interaction has mostly been studied in the solid state, and in contrast to the ubiquitous and much more common hydrogen bonds, very few applications in solution have been reported. More specifically, despite the various analogies between hydrogen bonds and halogen bonds, use of the latter in organocatalysis has only been reported for one case, namely the reduction of quinoline derivatives.[2]

The aim of our investigations is to develop applications for halogen bonds in organic synthesis and organocatalysis. A special focus of our research efforts is on the rational design of novel multidentate halogen bond donors (i.e., Lewis acids) R-X.

Since it is well known that halides as Lewis bases form strong halogen bonds in the solid state, we sought to use strong halogen bond donors for the abstraction of halide leaving groups from organic substrates. Recently we could demonstrate that certain dicationic halogen bond donors are able to activate the carbon-bromine bond of benzhydryl bromide and related substrates.[3] The bidentate halogen bond donors employed are based on iodoimidazolium groups and can be prepared easily and in high yield. In comparative experiments with non-iodinated reference compounds as well as with Broensted acids, strong indications were obtained that the activation of the carbon-bromine bond can indeed be ascribed to halogen bonding.

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Keywords: *Halogens; Noncovalent interactions; Solvolysis; Synthetic methods;*

P-0338

SELF-ASSEMBLY OF POLYNUCLEAR SUPRAMOLECULAR METAL-COMPLEXES CONTAINING PYRIDINE-LIGANDS

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Self-assembly, a concept often seen in nature has become a useful strategy to form metallosupramolecular assemblies, ranging from simple helices to large ball-shaped cavities. These complexes can even find application as molecular reaction vessels.[1]

Through several synthetic steps we have synthesized ligands with pyridine as the metal-binding unit, e.g. 9,9'-spirobifluorene-based ligands[2] and ligands containing two different metal-binding units, which are able to form discrete complexes with different metal-ions through self-assembly. These form homonuclear helices or heteronuclear trigonal bipyramids, respectively, when combined with suitable metal-ions.

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Keywords: *supramolecular chemistry; self-assembly; metal-organic frameworks;*

P-0339

HIGHLY FLUORESCENT PENTACYCLIC FRAMEWORK THROUGH A CASCADE PROCESS

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This presentation describes the synthesis of a new family of pentacyclic chromophore whose fluorescence properties can be modulated according to the functional groups present in the molecule. These chromophores were obtained through a cascade reaction between 2-formylbenzene boronic acid and 2,5-dihalopyridines. The cascade process was initiated by a palladium-catalyzed cross-coupling reaction and was followed by two successive nucleophilic cyclizations; the first cyclization performed on the pyridine nitrogen and the second occurred regioselectively on the adjacent carbon atom. This new cascade reaction allowed the formation of a pentacycle as a single regioisomer with four new bonds and two contiguous stereocenters with trans relationships. In addition, preliminary studies have shown that these polycyclic compounds have excellent fluorescence properties that should enable us to extend the scope of these new chromophores to the medical field and molecular electronics.

Keywords: *Chromophores; Diastereoselectivity; Fluorescence; Nitrogen heterocycles; Fused-ring systems;*

P-0340

HETEROGENEOUS PHOTOCATALYSIS IN ORGANIC SYNTHESIS.

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Visible light photocatalysis is a topic of increasing interest for many applications. One way of utilizing the visible range of the solar spectra is the combination of organo- an photoredox catalysis as pioneered by MacMillan[1a]. Using MacMillan's catalyst in conjunction with inorganic semiconductors as sensitizers, we have investigated the asymmetric C-C coupling of octanal with different bromo-substrates[1].

The range of investigated semiconductors includes the well-known blank TiO_2 (P25), dye-sensitized TiO_2 (**1**) as well as novel $PbBiO_2Br$ semiconductors. The $PbBiO_2Br$ semiconductor was used in two modifications – nanoparticles and bulk material, which have band gaps of 2.56 eV and 2.47 eV, respectively and can be irradiated with 440 nm LEDs. TiO_2 was sensitized by the Phos-Texas Red dye, which was immobilized on the surface and showed an absorption maximum at 560 nm.

The products could be obtained in good to very good yields of up to 84 % ($PbBiO_2Br$ *nano*/2-bromodiethylmalonate) and with excellent enantioselectivities of up to 96% ($PbBiO_2Br$ *nano*/bromoacetophenon)[2].

Other C-C bond formation reactions are under investigations in our group.

Acknowledgement: *Financial support: DFG: GRK 1626 – Chemical Photocatalysis.*

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Keywords: *heterogeneous photocatalysis; visible-light photocatalysis;*

P-0341

CONTINUOUS METATHESIS UNDER LIQUID-LIQUID CONDITIONS USING A DICATIONIC RU-ALKYLIDENE IN MONOLITH-SUPPORTED IONIC LIQUIDS

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Supported ionic liquid phase (SILP) catalysis has proven valid for various reactions7[1]. There, the catalyst is immobilized within a thin layer of an ionic liquid, which is coating a highly porous support material. We have developed a catalytic system for continuous metathesis-reactions, based on porous ROMP-derived polymeric monoliths, whose structures can be varied precisely with high reproducibility [2]. Following, the monoliths` surface was functionalized by grafting an ammonium-based monomer. Hereupon thin layers of the ionic liquid [BDMIM$^+$BF^{4-}] were immobilized which contained the novel dicationic Ru-alkylidene complex [Ru(DMF)$_3$(IMesH$_2$)(=CH-2-(2-PrO)-C$_6$H$_4$)]$^{2+}$(BF^{4-})$_2$]. Beside the primary objective to gain catalyst-free products, our concept enables continuous product formation using *two liquid* phases, i.e. one supported and a second continuous one, simply by cycling reactants through a monolithic support containing a suitable catalyst dissolved in an ionic liquid. Our catalytic system has proven valid for several biphasic (l-l), continuous metathesis reactions at a multitude of different flow rates and temperatures. For instance, the ring-closing-metathesis (RCM) of neat 1,7-octadiene as well as the RCM of *N,N*-diallyl trifluoroacetamide and diethyl diallyl malonate where heptane served as non-polar mobile phase, have been investigated in detail. Furthermore, the system was applied to the self-metathesis of methyl oleate. High turnover numbers and an exceptionally low catalyst leaching ($\leq$ 0.1% with respect to the initial amount of catalyst present in the IL phase) were observed. The fact, that a biphasic liquid/liquid system is used definitely widens the range of potentially accessible substrates. Moreover, the facile recycling of the monolithic support by flushing with, e.g., methanol, represents an additional advantage [3].

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Keywords: *Metathesis; Ruthenium; Immobilization; Mesoporous materials; Ionic liquids;*

P-0342

SHAPE-PERSISTENT LINEAR, KINKED, AND CYCLIC OLIGO(PHENYLENE-ETHYNYLENE-BUTADIYNYLENE)S: SELF-ASSEMBLED MONOLAYERS

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Self-assembled monolayers (SAMs) of rigid oligomers, particularly phenylene-ethynylene-butadiynylenes at the HOPG/TCB interface, are studied by scanning tunneling microscopy (STM) with submolecular resolution. Substitution of the terminating acetylene functions of the linear oligomers with polar 3-cyanopropyl dimethyl silyl groups leads to a 2D phase separation and defined rod-rod interactions, which determine the packing distances between the rigid rods. The results stimulated the connection of rigid rods via septiarylene clamp units. They covalently link two rigid rod units and define the intramolecular rod-rod distance that matches the alkoxy substituent chain lengths. The systems can be described as half-ring structures of two rigid rods that are connected *via* a rotatable joint unit. These acetylene-terminated half-ring structures are also oligomerized under Cu and Pd catalysis to yield defined acyclic and cyclic oligomers. Detailed STM studies decode the molecular origin of the surface patterning of such systems. The dodecyloxy side chains are adsorbed along the HOPG main axes and, together with the alkoxy backbone angle, determine the adsorption direction of the adlayers.

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Keywords: *self-assembled monolayers; scanning tunneling microscopy; shape-persistent molecules; solid/liquid interface; freely rotating chains;*

P-0343

NEW DIMERS OF BENZENE TRIAMIDE FOR HIGH ORGANIZATION IN LIQUID CRYSTAL MESOPHASES

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Discotic Liquid Crystals (DLc's) are well known in the field of organic materials [1], due to their interesting properties like 1D charge transport [2, 3]. Reducing the degree of freedom by making dimers has been shown to increase the conductivity [4]. Our aim is to use an aromatic linker as a probe to study the intermolecular self-assembly. The synthesis of the discogenic monomeric precursor was completed, showing mesomorphic proprieties.

Our attention is now focused on the design and screening of different types of aromatic linkers, in order to provide a rational understanding of the self-assembly in a discotic liquid crystal systems.

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Keywords: *Liquid Crystals; Materials scienc; Self-assembl; Dimerization; Hydrogen bond;*

P-0344

RED LIGHT EMITTING SYSTEM BASED ON AGGREGATION OF DONOR-ACCEPTOR DYES IN POLAR WATER MEDIA

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Red light emitting dyes have been of interest in view of their application as biological materials such as bioprobes and biosensors, because the red light emision is visible to the naked eye in an optical window. One of the simple strategies for the creation of the red light emitting dyes is based on a combination of electron-donor and electron-acceptor moieties. However, in a polar water system, the red light emission is quenched significantly by solvation of the polar water molecules. We have thought that the solvation-induced quenching can be restricted by the self-assembled aggregation of the donor-acceptor molecules.

In this study, we have demonstrated that the strategy actually worked for a series of triphenylamine-benzothiadiazole donor-acceptor molecules. In a THF/water mixture solution, the red light emission was quenched by the solvation in a low water volume. In contrast, in a high water volume, the red light emission was recovered and enhanced upon the aggregate formation of the donor-acceptor molecules; a high quantum yield up to 0.8 was achieved. The present emissive aggregate system worked even at the low concentration of 1×10^{-10} M. The strong red light emission is attributed to the restriction of the solvation-induced quenching, because the inside of the formed aggregates is less polar than that of the outside. The red light emitting aggregates were characterized by absorption and fluorescence spectroscopy, dynamic light scattering, atomic force microscopy, and X-ray diffraction analyses. The present result will provide a new strategy for the creation of a red light emitting aggregate system based on the simple combination of an electron-accepting core and electron-donating amino moieties.

Keywords: *emission; aggregation; donor-acceptor;*

P-0345

SYNTHESIS AND CHARACTERIZATION OF SIDE-CHAIN OXAZOLINE-STYRENE COPOLYMERS BEARING PHOTORESPONSIVE AZO-DYE

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The importance given to azo-polymers, in the last two decades or so, it is mainly because of azobenzene reversible *trans-cis* photoisomerization that enables to control changes over a variety of properties by means of light as an external stimulus[1]. Therefore, azo-polymers can be used in many interesting applications, varying from optical components and lithography to sensors and smart materials[2]. Each application asks for specific requirements. Hence, the type of polymer matrix and azo-dye, chromophore load and nature of bonding to the polymer matrix must be well-chosen and optimized[3].

This paper depicts the synthesis and characterization of new polymeric structures, in which a side-chain azo-moiety was attached on poly(oxazoline) and poly(oxazoline-co-styrene)s by ring-opening addition of dye's carboxyl group to the oxazoline cycle. The UV spectroscopy confirmed the quantitative addition of 4-((4(diethylamino)phenyl) diazenyl) benzoic acid to the oxazoline rings. The composition of products was controlled through co-monomers feed ratio, and estimated by means of ^{1}H-NMR spectroscopy and elemental analysis. Furthermore, a kinetic treatment using an integral method, revealed statistical copolymerization tendency of 2-isopropenyl-2-oxazoline with styrene in dichlorobenzene at 65°C. Both the substrates and azo-polymers exhibited good thermal stabilities and glass transition temperatures.

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Keywords: *2-oxazolines; azobenzene; polymer; cis-trans isomerization; photoresponsive behavior;*

P-0346

ISOMERIZATION KINETICS OF 2,4-SUBSTITUTED AZOBENZENES AND RELATED AZO-POLYMETHACRYLATES

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The *trans-cis-trans* photo-isomerization of azobenzenes containing-polymers allows fine-tuning of the optical response for holographic memories[1], optical storage data[2], or actuators[3]. Considerable research has gone into elongating the *cis* lifetime, with the goal of creating bistable photoswitchable systems. Depending on the substitution pattern and local environment, the electronic push and pull structures, such as pseudo-stilbenes and aminoazobenzenes can isomerize from *cis* configuration back into *trans*configuration very quickly at room temperature. However, the thermal *cis-trans* isomerization in azobenzene-type molecules is relatively slow, and it is even possible to elongate the *cis* isomer lifetime to years, if bulky substituents are introduced to hinder the thermal relaxation[4]. Understanding the relationship between molecular structure and photo-responsive behavior represents one of the most important issues in order to gain control over the response time.

In this paper, the *trans-cis-trans* isomerization kinetics of four 2,4-nitro/cyan substituted azobenzenes and related poly(methyl methacrylate) copolymers (having the azobenzene moiety in the side-chain)[5], is carried out through UV-Vis and ^{1}H NMR spectroscopy. Different isomerization behaviour is evidenced due to particular substitution pattern of each azobenzene derivative.

Aknowledgements: *The present work was supported by a grant of the Romanian National Authority for Scientific Research, CNCS–UEFISCDI, project number PN-II-RU-PD-2011-3-0063.*

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Keywords: *azobenzene; isomerization; polymers; NLO;*

P-0347

SYNTHESIS OF STEROID-TRILOBOLIDE CLICKATES FOR BIOLOGICAL STUDIES

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In this contribution synthesis of short series of conjugated natural products concerned to steroids and trilobolide (TB) is described. Trilobolide is a sesquiterpene lactone which was previously found to have an inhibition activity of sarco/endoplasmic reticulum Ca^{2+}-ATPase (SERCA). Also, it has been demonstrated that TB can serve as an immunostimulatory agent. Estradiol, testosterone, pregnendiol and dihydroxyandrosten were used as motive of steroidal moiety. These steroids as relatively lipophilic compounds may modify its biological availability and transport, moreover, fundamental steroidal skeletons are recognized by nuclear receptors in the nucleus of the cell. In this work TB is transformed at C-6 position to 5-azidovalerate. This structure serve as a building block for successive click reaction with ethynylated steroids. For comparison, steroids were also clicked with 5-azidovaleric acid to give corresponding trilobolide attached moieties. These compounds are now given for biological screens and tests to give new information about general behavior of such compounds.

Keywords: *trilobolide; steroids; click chemistry;*

P-0348

ANION BINDING PROPERTIES OF A SALOPHEN ZINC CHELATE / BILE ACID CONJUGATE INCORPORATED INTO CTABR MICELLES

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Metal complexes are excellent Lewis acidic binding sites for anions. In particular, Salophen-Metal complexes are extensively studied species, which have been successfully employed as receptors, catalysts, and carriers.[1] Bile acids are amphiphilic molecules found in the bile of mammals. They play many important biological functions, as in the metabolism of lipids for their ability to form mixed micelles, which interact with lipid bilayers of biological membranes and mediate transport of lipophilic compounds through the intestinal membrane.[2] We envisaged that, by combining the above described two structural units into one single entity, we could obtain a Metal-Salophen/Bile Acid conjugate possessing novel properties in terms of anion binding and transport. ^1H NMR and UV-vis studies demonstrate that the Zn-chelate, **1**, binds anions in DMSO, but the addition of 10% water severely hampers the binding. More importantly, the bile acid moieties in **1** render it capable of being incorporated into CTAB micelles. Using CTABr micelles as carriers for anion receptors is indeed a convenient way to test their anion binding properties in water.[3] Under such conditions, **1** is able to bind phosphate with a relatively high affinity (K ca. 500 M^{-1}). TEM microscopy and Dynamic Light Scattering studies highlight the influence that **1** and anions have on the size and shape of the CTABr micelles. These are important aspects that must be considered to fully evaluate the binding properties of the Zn-chelate / CTABr supramolecular system which resulted in being an efficient anion binder in the highly competitive water medium.

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Keywords: *micelles; click chemistry; anions; UV/Vis spectroscopy; Steroids;*

P-0349

RECYCLABLE POLYMER-COATED MAGNETIC NANOBEADS

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Chromatographic purification often is the limiting part of library syntheses and industrial high throughput processes due to high consumption of time and solvents. In order to avoid this bottleneck, polymer based reagents and scavengers have been developed, which enable easier purification through filtration.[1] However, filtration systems often suffer from membrane fouling and require energy-intensive pumping. As an alternative, highly magnetic nanoparticles combine high surface area with the benefit of agitation and separation via an external magnetic field.[2] Carbon coated cobalt and iron nanobeads were functionalized with norbornene tags followed by activation with Grubbs 2nd generation catalyst and subsequent grafting of *N*-hydroxysuccinimide ROMPgels on the surface.[3] This approach allowed an easy tuning of the polymer by variation of the amount of monomer. The high loading hybrid magnetic material (2–3 mmol/g) was then applied in the acylation of various amines. Rapid and operationally simple magnetic decantation resulted in pure products with high yields. The nanoparticles were efficiently reused in more than five consecutive cycles.

Alternatively, Co/C and Fe/C nanoparticles with a high loading of benzylchloride moieties were synthesized via radical polymerization on the surface of the nanomagnets. A "click"-reaction was utilized to tether cyclen azamacrocycles to the polymer coated nanobeads followed by complexation with zinc(II). Complete extraction of riboflavin (vitamin B2) from aqueous solutions and a commercial vitamin tablet at pH 7.4 and subsequent release at pH 3.6 was achieved for more than five consecutive cycles without considerable loss of activity.

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Keywords: *Nanoparticles; Magnetic properties; Polymers; Acylation; Analytical methods;*

P-0350

SYNTHESIS OF ILS WITH BORON-CONTAINING COUNTER-IONS

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Ionic Liquids (ILs) have found wide spread and steadily expanding application, as solvents, in catalysis, as extraction material or as electrolyte in batteries. Most of them require ILs which are liquid at room temperature. We describe in our study TAAILs (Tuneable Aryl Alkyl Ionic Liquids) with novel counter-ions. TAAILs are imidazolium-based cations with variable alkyl chain lengths or substituents on the aryl ring. In comparison to the frequently used Bis(trifluoromethanesulfonimide) we investigate boron-containing non-coordinating counter-ions.

Keywords: *Ionic liquids; Boron;*

P-0351

REVERSIBLY SWITCHABLE WETTABILITY THROUGH MODULATING SURFACE CHARACTERISTICS

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Polyeletrolytes are negatively or positively charged polymers with repeating units that combine with an individual counterion and experience potentially strong electrostatic interactions due to their multiple charges. In particular, charged polymers exhibit diverse physicochemical properties depending on the natures of their counterions. The exchange of counterions connected with charged units induces significant changes in the chemical architectures and properties of polyelectrolytes as well as in their unique functions. Moreover, since ion-exchange reactions enable the collection of specific salts from electrolyte solutions through the trapping and releasing reactions between the ions, polyelectrolytes have been widely used in a number of industrial fields, such as the desalination of sew water, demineralization, water softening, polymer electrolyte fuel cells (PEFCs), pharmaceutics, sensors, and carbohydrate refining. In particular, by adsorbing ion-exchangeable polymers onto nanostructures surfaces, the ion-paring interaction leads to changes in surface characteristics through the capture of specific ions with various polarities and hydration energies by selection of the appropriate counterions, and thus plays a pivotal role in the development of intelligent devices such as smart windows, humidity sensors, oil separators. Multi-scale surface nanostructures with a large surface-to-volume ratio are an essential prerequisite for maximizing the performance of such smart devices and systems, because the rate of the ion exchange process depends intrinsically on the specific surface area. In this study, we developed a multifunctional electrospun polymeric nanofiber web with switchable superhydrophobicity as well as oleophobicity via clicking counterions. To produce this smart fabric, we used a strategy that combines electrospinning to fabricate nanofibrous templates with nanopores a d a simple coating of the polyelectrolyte that can exchange counterions with various hydration energies.

Keywords: *Exchange interactions; polymers; Surface chemistry; Nanostructures; Hydrophobic effect;*

P-0352

SYNTHESIS OF NEW ANTITUBERCULOTICS DERIVED FROM BENZYLSULFANYLHETEROAROMATES

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The search for effective antituberculotics remains current and very important topic because a lot of patients are infected by *Mycobacterium tuberculosis* and their number is increasing.

It was showed that benzylsulfanyl derivatives of benzimidazoles, benzothiazoles and benzoxazoles possessed the highest *in vitro* antitubercular activity when the benzylsulfanyl moiety carries the electron-withdrawing substituents [1, 2].

Our work focused on the synthesis of new potential antituberculotics based on benzylsulfanylheteroaromates. A series of 1-alkyl/aryl-5-benzylsulfanyl-1*H*-tetrazole with electron-withdrawing substituents on the benzylsulfanyl moiety was prepared. We found that substituents in the position 1 have only low influence on the antimycobacterial activities.

The series of selenium, oxygen, sulfinyl and sulfonyl isosteric analogues of 1-alkyl/aryl-5-benzylsulfanyl-1*H*-tetrazole were synthesized. The oxygen and selenium derivatives showed the activities like the sulfanyltetrazoles, while sulfinyl and sulfonyl analogues had lower activities.

We also synthesized the series of 2,5-disubstituted 1,3,4-oxa- and 1,3,4-thiadiazoles with substituted benzylsulfanyl moiety. These compounds showed higher activities than tetrazole analogues.

It is necessary to note that some of the selected compounds showed only low toxicity against isolated human hepatocytes as well as JEG3 cells.

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Keywords: *Medicinal chemistry; Heterocycles;*

P-0353

A NEW APPROACH TO PREPARATION OF CONDUCTIVE COMPOSITES BASED ON POLYANILINE

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Polyaniline takes a special position among conducting materials due to the simplicity of its synthesis, ease of carrying out reversible processes of doping – dedoping and a range of excellent properties. However, the rigidity of the polymer chain and, consequently, infusibility and insolubility in most organic solvents, as well as the lack of stability in the operating conditions are the serious obstacles to its practical application. The solution to this problem is the creation of polymeric composite materials based on PANI, characterized by good electrical and mechanical properties.

The goal of this research work is the development of a new original method of preparation polymer-polymer composites, in which microlayers of PANI are distributed in the inert matrix of polystyrene (PS), which provides high mechanical properties and stability of electrophysical characteristics. PANI-PS composites were prepared by border-line polymerization of aniline at the interface of immiscible liquid phases – aqueous solution of aniline and oxidant and organic solution of PS. Under intensive stirring the forming PANI microlayers encapsulate drops of PS solution. After the separation of the aqueous phase, as a result of destruction of the microcapsules, a new composite material, in which microlayers of PANI with length 1-3 μm and thickness ~0,2 μm are dispersed in the volume of solid inert PS matrix, is being formed. PANI microlayers are characterized by a high degree of homogeneity both in terms of morphology and chemical structure as follows from electron microscopy and FTIR surface reflection data. Electrophysical properties of the obtained composites were studied. Depending on preparation conditions conductivity falls insite the limits of 10^{-3}-10 Sm/cm.

Obtained polymer-polymer composites are of advantage for application in organic electronics, electrochromic systems, as antistatic coatings and protecting shields from electromagnetic and radioactive emission.

Keywords: *conducting materials; polymerization; electron microscopy;*

P-0354

ORDERED HYBRID THIN FILMS FROM POLY(3-HEXYLTHIOPHENE) BLOCK COPOLYMERS FOR PHOTOVOLTAIC APPLICATIONS

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Thin film hybrid photovoltaics, which include organic donor and inorganic acceptor components, are attractive due to higher adsorption coefficients, more desirable mechanical properties and less expensive processing. Despite these advantages, hybrid thin film devices have shown limited efficiency due to poor charge separation and extensive charge recombination. Control of film morphology at the nanoscale and of the organic/inorganic interface is essential for further improvements in device efficiency. The present work seeks to yield well-defined film architectures by taking advantage of the phase separation of block copolymer films. Block copolymers of poly(3-hexyl thiophene) P3HT were prepared via reversible addition-fragmentation chain transfer (RAFT) polymerization. A novel P3HT macroRAFT agent was designed to maintain a trithiocarbonate end group after the preparation of a block copolymer. The P3HT macroRAFT agent was utilized to prepare rod-coil block copolymers with poly(styrene) and poly(*tert*-butylacrlyate). The trithiocarbonate end group was subsequently used for attachment of the P3HT homopolymer and the block copolymers to inorganic surfaces. This utility was demonstrated by attaching P3HT polymer to gold nanorods, which were then incorporated into polymer films. The location of the nanoparticles in the thin films can be controlled by the polymer on the nanoparticle surface.

Keywords: *Block Copolymers; Self assembly; Nanostructures;*

P-0355

TRANSIENT AND SWITCHABLE PROTECTION OF DNA AGAINST CLEAVAGE BY RESTRICTION ENDONUCLEASES

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The restriction endonucleases type II (REs) are very important in the manipulation of DNA.[1] In previous studies was found that several of these showed a high tolerance to the presence of alkynyl group but not to more bulky groups at position 7 of 7-deazaadenine.[2]

Our method utilises the trialkylsilyl protected 7-ethynyl-7-deazaadenine as a bulky substitution of 7-deazaA which protects the DNA against cleavage by REs and after removal of trialkylsilyl group the afforded 7-ethynyl-7-deazaadenine is tolerated by REs and thus, DNA could be cleaved.[3]

.We tested three trialkylsilyl protective groups: trimethylsilyl, triethylsilyl (TES) and triisopropylsilyl. According to the experimental results the most suitable protecting group of 7-ethynyl-7-deazaadenine for our method is TES. The modified nucleoside triphosphate **dA^{TESE}TP** is very good substrate for DNA polymerases in primer extension experiment and the construction of large DNA by PCR. The resulting modified DNA is fully protected against cleavage by REs. Another key advantage of using the TES protecting group is the ease at which it can be removed by the treatment with aqueous ammonia, which is simply evaporated and without any further purification DNA could be cleaved by REs.

This approach may find applications in manipulation of DNA sequences, where target sequences for some REs must be distinguished.

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Keywords: *DNA cleavage; Nucleic acids;*

P-0356

STUDY ON THE PHYSICAL PROPERTIES AND CRYSTALLIZATION KINETICS OF MODIFIED PP COMPOSITES WITH NANOFILLER

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Commercial Polypropylene (PP) exhibits low melt and impact strengths, which limit its use in foaming and automotive applications. The melt strength of PP can be improved by controlling the molecular weight property and introducing long-chain branches (LCBs). Control of the crystal growth rate is crucial for the preparation of modified PP (m-PP) with LCB because the crystallization kinetics affect the polymer processing.

The objective of this study is to determine the effects of LCB and loading nano-filler on the physical properties and the crystallization kinetics of m-PP.

M-PPs were prepared by melt grafting and electron beam irradiation, and m-PP composites with nano-filler were fabricated by adding 1–7 wt% filler using a mini-compounder at 200 °C. Layered silicate, carbon nano-tube (CNT), and graphene were used as the nano filler. There was no difference in the spectra of m-PP and pure PP whcih were measured by FT-IR and ^{1}H-NMR. To check branch reaction, the branching level was calculated by zero-shear viscosity and molecular property. The rheological properties were monitored using an oscillatory viscometer (Anton Paar, MCR 301). The crystallization behavior of m-PP and the nanocomposites were analyzed using the isothermal and non-isothermal kinetic process proposed by Avrami and Ozawa, respectively. The enhanced melt strength can be interpreted from the observation that the loading of nano-filler and introducing LCB into PP enhances its solid-like properties in the PP melts. The dispersion of nano-filler was verified by transmission electron microscope (TEM) and X-ray diffraction (XRD). The melt stregnths of PP were measured by Instron capillary rheometer with tensiometer.

Keywords: *polypropylene; long-chain branch; nano-filler; nanocomposite; crystallization;*

P-0357

TEMPLATE-DIRECTED SYNTHESIS, STRUCTURE, AND SUPRAMOLECULAR CHEMISTRY OF CONJUGATED PORPHYRIN NANORINGS

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Fully π-conjugated porphyrin nanorings combine an end-free π-system with well-defined size and shape. They provide models for testing our understanding of light harvesting in natural photosynthetic systems, and they may lead to the creation of new functional materials. Here we report on such systems consisting of 6, 8, 12, 18 and 24 porphyrin units, respectively, that are linked by butadiyne-bridges. These structures have been approached by template-directed synthesis. The formation of the larger rings illustrates the scope for Vernier templating as an efficient tool for the synthesis of monodisperse molecules of unprecedented sizes. Investigations of the structure and supramolecular chemistry of the nanorings are presented.

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Keywords: *Conjugation; Nanostructures; Porphyrinoids; Supramolecular Chemistry; Template Synthesis;*

P-0358

4,4'-AZO-BIS(HALOPYRIDINIUM) DERIVATIVES: STRONG MULTIDENTATE HALOGEN-BOND DONORS WITH A REDOX-ACTIVE CORE

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Recently, a growing number of studies describe applications of halogen bonds (XBs), which are non-covalent interactions between lewis-acidic halogen atoms in compounds R-X (X=Cl, Br, I) and a Lewis base,[1] in solution (e.g. for anion recognition and organocatalysis [2]).

For these applications, the formation of strong XBs is a necessity, which can be achieved by making the rest R sufficiently electronegative. The usage of cationic moieties attached to the halogen atom provides this electron withdrawal. In the course of our investigations, we recently reported the activation of the carbon-bromine bond in benzhydryl bromide by *imidazolium*-based halogen bond donors (XB-donors).[3] Based on X-ray structural analyses of halo*pyridinium*moieties, which also form strong XBs with halides,[4] we synthesized new azo-bridged bis(halopyridinium) compounds, firstly to extend the XB-based activation of carbon-heteroatom bonds to further multidentate XB-donors and secondly to investigate their activation potential in the mentioned benchmark reaction by comparing it to the activation potential of the *imidazolium*-based XB-donors. The azo bridge, which also constitutes a built-in redox option, was chosen as a short and easy to install junction for the connection of two halopyridinium fragments. Several X-ray structural analyses of these new XB-donors could be obtained and NMR titration experiments showed a higher efficiency of these activators in our benchmark reaction.[5]

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Keywords: *Halogens; Solvolysis; Noncovalent interactions; Azo compounds;*

P-0359

MOLECULAR SWITCHES FOR AFM MEASUREMENTS

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Azobenzenes are the prototype of switchable molecules.[1] Therefore, the mechanical work of their photoisomerization shall be determined quantitatively. Azobenzene derivatives shall be attached covalently between a glass surface and a cantilever in an atomic force microscope (AFM).

New azobiphenyl molecules to amplify the effective distance change during the E,Z-isomerization will be presented. This shall lead to a better signal-to-noise ratio due to increased change of length.[2] The azobiphenyls are substituted with methylgroups to improve solubility. All synthesis were done by an oxidative copper(II)-catalyzed coupling reaction in combination with a Suzuki reaction.

In solution, the switching behavior of azobenzenes and azobiphenyles was examined by NMR and UV/Vis spectroscopy. The amount of cis isomer was determined by NMR spectroscopy. The reversibility of switching was investigated by UV/Vis spectroscopy. All investigated molecules showed E,Z-isomerization and sufficiently long half-life times.

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Keywords: *Azo compounds; Photochemistry; Oxidation;*

P-0360

VISIBLE LIGHT PHOTOREDOX CATALYSIS WITH N-A-RADICALS AS INTERMEDIATES

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In recent years many discoveries were made in the field of photochemistry mediated by visible light. Light is inexpensive and readily available worldwide. It is not polluting the environment and can transfer energy under mild reaction conditions. Applying the concept of photoredox catalysis with visible light, ruthenium(II) and iridium(III) complexes proved to be versatile catalysts due to their good charge separation abilities and redox properties.[1] The transition metal complex acts hereby as an electron shuttle which transfers electrons from a donor to an acceptor or *vice versa*.

Due to our progress in the field of photocatalytical debromination reactions we started to investigate photocatalytical conjugate addition reactions.[2] In the course of our studies, we discovered that *tert.* amines can be oxidized by photoredox catalysts to an amine located radical cation which rearranges to a N-α-radical under loss of an proton. This radical than attacks an enone system and forms the conjugate addition product subsequently.[3] *N*-Phenyltetrahydroisoquinoline species proofed to be the most suitable *tert.* amine. On the other hand, most enone systems are applicable in this reaction and lead to the expected conjugate addition products in moderate to good yields.

Our current studies focus on expanding the scope and increasing the yield of the reaction. Especially the functionalization of different *tert.* amines would be of interest due to their regular appearance in natural products and pharmaceutical drugs. We are also concentrated on the development of a selective photocatalytic conjugate addition.

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Keywords: *photocatalysis; conjugate addition; photoredox catalysis;*

P-0361

PALLADIUM-CATALYZED DIRECT C–H BOND FUNCTIONALIZATIONS

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Heteroatom-substituted secondary phosphine oxides (HASPO) have emerged as efficient preligands for transition metal-catalyzed cross-coupling reactions.[1, 2] Recently, we synthesized well-defined air-stable palladium complexes derived from (HA)SPO-preligands, which turned out to be versatile catalysts for efficient Kumada-Corriu cross-coupling reactions of unactivated (hetero)aryl- and alkenyl tosylates with an improved catalytic activity as compared to the corresponding in-situ generated catalysts.[3]

These complexes were found to be highly active catalysts in environmentally benign direct C–H bond arylations and benzylations of various azoles.[5, 6] Moreover, direct C–H bond alkynylations of heteroarenes were accomplished with inexpensive *gem*-dichloroalkenes as user-friendly electrophiles.[7]

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Keywords: *Cross-coupling; C-H activation; Heterocycles; Homogeneous catalysis; Palladium;*

P-0362

SYNTHESIS AND ANTI-INFLUENZA VIRUS ACTIVITY OF N-ARYLATED BETA-AMIDOAMIDINES STRUCTURALLY RELATED TO NATURAL ANTIBIOTIC AMIDINOMYCIN

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Influenza infections are responsible for many million cases of illness and up to a half of million deaths per year. Despite of availability of antiviral drugs against influenza infections, the emergence of viral resistance to existing antiviral drugs emphasizes the demand for development of new antiviral drugs against influenza. Naturally occurring Amidinomycin and Noformycyn represent a b-amidoamidine type of antibiotics, which is of considerable chemotherapeutic interest due to a wide range of antibacterial and antiviral activity. However these compounds and their close derivatives appeared to possess high level of toxicity.

In this work, we report an efficient 3-step synthesis of racemic N-arylated b-amidoamidines **4**, which being non-toxic revealed an antiviral potency against influenza virus A (H3N2) *in vitro*. Indeed, reactions of methacryloyl anilides **1** with PCl_5 at rt smoothly afforded the imidoyl chlorides **2**, which upon treatment with 2 equiv of the same aniline gave the corresponding N-arylated b-aminoamidines **3** as hydrochlorides. The salts **3** were converted to free bases, the latter were mono-acylated with acyl chlorides at the less nucleophilic b-amino-group to give the b-amidoamidines **4**. A plausible mechanism for this mono-functionalization of the less reactive reaction center through the acyl-group migration will be briefly discussed.

The b-aminoamidines **3** and the b-amidoamidines **4**, being tested *in vitro* against influenza virus A/St.Peterburg/34/72 (H3N2) exhibited different level of antiviral activity and cytotoxicity. For example, while N-phenyl-substituted b-aminoamidine **3** (HCl-salt) is totally inactive and extensively cytotoxic (MCC_{50} 85 mmol), it's b-N-acetyl derivative **4a** is twice less toxic and considerably active (IC_{50} 68 mmol). An elongation of the alkyl chain in **4c** ($R = n\text{-}C_8H_{17}$) resulted in significant antiviral potency ((IC_{50} 0.95 mmol) accompanied by a modest toxicity (MCC_{50} 250 mmol). A considerable *in vivo* protective activity of long alkyl chain **4** against experimental influenza virus A/Aichi/68 (H3N2) infection was also observed.

Keywords: *amination; Michael addition; acylation; cyclization; antiviral agents;*

P-0363

SYNTHESIS OF NEW XANTHENE DERIVATIVES FOR LABELING OF BIOMOLECULES

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Xanthene dyes, particularly fluorescein are a well known class of fluorescent dyes, which have widespread applications in natural sciences. The synthesis of xanthene derivatives *via* acid catalyzed condensation of substituted phenols with phthalic anhydride, to afford the required derivatives, is well established. The high temperature, harsh reaction conditions and often lower yields make this method less convenient. The synthesis of xanthene dyes by direct modification of the fluorophore moiety is a great option to avoid the standard procedure. Our new synthetic strategy for preparation of novel asymmetric xanthene dyes *via* direct conversion of hydroxyl groups on 3'- and 6'-positions into leaving groups by mesylation is reported. It was discovered that 3',6'-dimesylated fluorescein undergo catalyst free nucleophilic aromatic substitution with sulfur nucleophiles. Additional this type of alteration of the fluorophore structure improved significantly its photostability. Not only 3',6'-mesylated fluorescein, but also 3',6'-mesylated 2',7'-dichloro, 4',5'-dibromo or 4',5',7'-tribromo derivatives of fluorescein are used as starting materials for preparation of these new fluorescent dyes.

This strategy provides novel fluorescent probes with the linker suitable to further modifications. The modifications of the linker enable to prepare fluorescein derivatives that can be used as fluorescent labels in peptides, oligonucleotides and for cell imaging. Especially new azido fluorescein derivatives are reported. They could be used for a “click” reaction with acetylene modified nucleosides and be incorporated into live cells during cellular transcription and translation.

Keywords: *Fluorescent probes; Sulfur; Synthesis design; Azides; Aromatic substitution;*

P-0364

PREPARATION OF NEW PUSH-PULL CHROMOPHORES WITH FERROCENE MOIETY

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Objective of this work was the synthesis of new push-pull chromophores, whose preparation has not yet been published. Ferrocene was used as donor group and N-methylimidazole-4,5-dicarbonitrile was used as acceptor group. Thiophene ring in combination with one or more multiple bonds was used as a p-linkage between donor and acceptor unit.

Target chromophores were synthesized by three to five step synthesis using mainly Heck, Sonogashira and Suzuki-Miyaura cross-coupling reactions and some others. Overall it was prepared twenty five intermediate products. It was ten final products obtained in high purity.

Structures and purity of the prepared compounds have been verified by basic analytical methods - GC/MS or LC/MS, ^{1}H and ^{13}C NMR, infrared spectroscopy and elemental analysis.

Acknowledgement: *This work was supported by the Grant Agency of the Czech Republic (P106/12/0392) and by the Ministry of Education, Youth and Sport of the Czech Republic.*

Keywords: *Push-pull chromphores; ferrocene; thiophene; N-methylimidazole-4,5-dicarbonitrile;*

P-0365

MOTIONAL AND CONSTITUTIONAL DYNAMICS OF IMINES

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The imine double bond possesses many interesting features: it can form reversibly from an aldehyde and amine eliminating a molecule of water, it is susceptible to attack with nucleophiles such as amines, performing imine exchange, and it responds to certain chemical stimuli such as pH, coordinating metals, etc.

These properties provide a good background for applications in Dynamic Covalent Chemistry (DCC). General demands in this field comprise of fast formation of dynamically interconverting species and rapid response towards physical and chemical stimuli which can occur in a vast range of applicable solvents, with a particular interest for aqueous solutions.

Salicylaldehyde and pyridine-2-carboxaldehyde have been identified as the most promising aldehydes for imine-based DCC. They form imines with high conversion and rate even in aqueous media and readily exchange with their amine counterparts.

Amines bearing more than one amino-group undergo both intermolecular and intramolecular exchange, wherein the rate of the former depends on concentration and the latter on distance between the two amino-groups.

The condensation of salicylaldehyde and ethylenediamine strongly prefers imine formation over the aminal form, making the aldehyde end-to-end displacement observable and quantifiable by VT-NMR. The rate of such displacement decreases rapidly with increasing chain length. Thus for a molecule of cadaverine, intramolecular exchange is not observed.

Extending the simplest aliphatic diamines to complex linear polyamines such as diethylenetriamine and triethylenetetramine, the very same behaviour is observed. Imine formation is predominant in solution and intramolecular end-to-end exchange is observed by 2D-EXSY. This exchange proceeds in a stepwise fashion by participation of the secondary nitrogens, giving rise to aminal intermediates, which is confirmed by kinetic studies, 2D NMR and molecular modeling of analogues without secondary nitrogens.

This interesting behaviour can be considered to be non-directional small molecule walking along a track, a remarkable observation found for first time with imines.

Keywords: *imine exchange; dynamic covalent chemistry; molecular dynamics; molecular motors;*

P-0366

SYNTHESIS OF THE TRICYCLIC CORE UNIT OF DISCODERMIDE

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The marine natural product discodermide was isolated for the first time in 1991 by Gunasekera and co-workers from the Caribbean marine sponge *Discodermia dissoluta.*[1] Discodermide belongs to the class of tetramic acid lactams and displays remarkable biological characteristics. It inhibits the in vitro proliferation of cultured murine P388 leukemia cells with an ICM of 0.3 µg/mL as well as the growth of *C. albicans* with an MIC of 12.5 µg/mL. Other members of this class are cylindramide, isolated from the Okinawan sponge *Halichondria cylindrata,*[2] or geodine A, recently isolated from the southern australian marine sponge *Geodia*.[3] Characteristic structural features of these compounds are the tetramic acid moiety and the substituted bicyclo[3.3.0]octane unit. In the case of discodermide the bicyclo[3.3.0]octane is replaced by the tricyclic dodecahydrocyclopent[a]indene unit. Compared to cylindramide, which was synthesized by Cramer in 2005,[4] discodermide is currently neither available by synthesis nor fermentation.

In the course of a total synthesis of discodermide, the tricyclic core unit, the dodecahydrocyclopent[a]indene, is synthesized in diastereomerically pure form prepared from readily available 1,5-cyclooctadiene. After cyclisomerization the obtained bicyclo[3.3.0]octane-2,6-dione is functionalized by copper-mediated 1,4- or magnesium-mediated 1,2-addition. The key step is an intramolecular aldol reaction to obtain the tricyclic core unit, which is then further functionalized.

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Keywords: *Natural products; Asymmetric synthesis; Grignard reaction;*

P-0367

TOTAL SYNTHESIS OF ARTELUDOVICINOLIDE A

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The total synthesis of natural products is of increasing interest since such molecules inherit a huge potential for biologically active compounds. Therefore, many plant extracts have been investigated to find new lead structures for novel effective drugs. Several members of the genus *Artemisia* have been widely used in traditional medicine in the northern hemisphere. Among the numerous sesquiterpene lactones discovered in *Artemisia ludoviciana*, the guaianolide Arteludovicinolide A was found.[1] It was shown that this compound exhibits significant antiinflammatory activity.[2]

The key step of the synthesis toward the γ-butyrolactone utilized a recently discovered synthetic intermediate, an α/β-chiral aldehyde which could be accessed in four simple steps from readily available starting materials: The enantio- and diastereoselective synthesis of the natural product started from furan-2-carboxylic ester by asymmetric cyclopropanation followed by ozonolysis and successive, highly diastereoselective Sakurai-allylation.[3] After some further synthetic manipulations, the α/β-chiral aldehyde was obtained in high yield. By reacting a lithiumorganyl with this aldehyde, the key structural element, a *trans*-substituted γ-butyrolactone was obtained. After introduction of the *exo*-methylene group via Eschenmoser`s salt followed by chemoselective Wacker oxidation the natural product was obtained in 10 linear steps and 2.9% overall yield.

The scope of the α/β-chiral aldehyde for the construction of diverse *trans*-substituted γ-butyrolactones has also been investigated. Thus, various substructures can be introduced in the lactone moiety by applying organometallic reagents.

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Keywords: *total synthesis; natural products; enantioselectivity; ketones; ozonolysis;*

P-0368

A GENERAL REGIOSELECTIVE APPROACH TO 2,4-DISUBSTITUTED PYRIMIDINE-5-YL C-2-DEOXYRIBONUCLEOSIDES

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C-nucleosides bearing hydrophobic aryl groups as nucleobase are interesting compounds with wide range of applications in chemical biology, for example in extension of the genetic alphabet.[1] There are several synthetic approaches to C-nucleosides, but none of them is truly general and many of them suffer from poor selectivity and low yields.[2]

A new modular synthesis of diverse 2,4-disubstituted pyrimidin-5-yl C-2'-deoxyribonucleosides by sequential regioselective reactions of 2,6-dichloropyrimidin-5-yl C-nucleoside was developed.[3, 4] The intermediate was prepared by the Heck coupling of 2,6-dichloro-5-iodopyrimidine with glycal followed by desilylation and reduction. Its mild nucleophilic substitutions, Fe-catalyzed cross-coupling with MeMgCl or Pd-catalyzed amination proceeded regioselectively at position 4. In second step position 2 was functionalised to prepare four series of diversely substitued derivatives.

In conclusion two-dimensional library of 2,4-disubstituted pyrimidine C-deoxyribonucleosides bearing two different substituents was prepared. Some of these nucleosides will be transformed to triphosphates and tested as substrates of DNA polymerases. These studies are now under way in our laboratory.

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Keywords: *nucleosides; cross-coupling; Heck reaction; nucleophilic aromatic substitution; regioselectivity;*

P-0369

CONVERSIONS OF PHOSPHONOMETHIONINE AND RELATED COMPOUNDS

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1-Aminoalkylphosphonic acids are structural analogs of natural amino acids, obtained by an isosteric substitution of the planar carboxylic group [C(O)OH] by the tetrahedral phosphonic function [$P(O)(OH)_2$]. In this class of amino acids the group of special interest present so called, the proteinogenic 1-aminoalkylphosphonic acids, in this phosphonomethionine (Met^P) and related compounds [1].

Phosphonomethionine – originally synthesized in 1980 [2], and its analogs - phosphonohomocysteine ($Hcys^P$) [2, 4] and phosphonocysteine (Cys^P) [3, 4], present the interesting subject for chemical [5–8] and biological [9] explorations.

In this communication, we present our results on the further sulfur functionalisation of this type of aminophosphonic acids, especially their *N*-methyl, and *N,N*-dimethyl derivatives.

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Keywords: *Aminoalkylphosphonic acids; Phosphonomethionine; Amino acids;*

P-0370

CRITICAL ASSESSMENT OF THE EFFICIENCY OF CHITOSAN-BASED MATERIALS AS POTENTIAL ORGANOCATALYSTS FOR C-C BOND FORMATION

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Since petrochemical-based feedstocks will be limited in future and are getting therefore much more expensive, cheap alternative sustainable resources like polysaccharides (e.g. chitosan, alginates, hyoluronic acid, carrageenan, cellulose, etc.) already play and will play a more important role in high-tech applications and industrial processes.[1] Beside such key advantages like biodegradability, biocompatibility and antibacterial activity, these materials are wide abundant on earth, offer a variety of functional groups and own in most cases chiral backbones.[2] Latter benefits qualify these compounds as potential organocatalysts in different organic transformations.

In this study the effectiveness of commercial available chitosan powder (CSP), air-dried chitosan hydrogel beads (ADCSHB) and neutral pH chitosan hydrogel beads (CSHB) as a green organocatalyst for different C-C bond forming reactions (i.e. aldol reaction, Knoevenagel condensation, nitroaldol (Henry) reaction and Michael addition) has been comprehensively evaluated. Reaction rates, conversions and selectivities were investigated in dependence of different input variables including size, pH and reactive surface of the beads, catalyst loading, temperature, molecular weight of the biopolymer, concentration, solvent system and molar ratio of reactants. Moreover, the chitosan-based materials were characterized by a variety of techniques including, among others, SEM, FT-IR, TGA and DSC.[3]

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Keywords: *chitosan; hydrogel; C-C bond formation; organocatalysis;*

P-0371

VISIBLE LIGHT PHOTOCATALYSIS – FLAVINS AS CATALYSTS IN ORGANIC REACTIONS

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Flavins are nature's beloved redox co-factors.[1] When irradiated by blue light, their ability to oxidize is dramatically increased and thus they can be used in photocatalysis.[2] They are easily accessible by synthesis and their properties can be tuned by substitution pattern.[3]

Recently we reported different organic reactions with vitamin B_2 derivatives as efficient photocatalysts.[4,5] The key step of the photocatalytic cycle is the formation of the triplet state of the flavin.[6] Based on the conclusions of these investigations we are now able to present some improved derivatives of this catalyst that yield higher triplet state populations due to heavy atom effect. These new photocatalysts accelerate the oxidation reactions and improve quantum yields.

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Keywords: *Photochemistry; Homogeneous Catalysis; Green Chemistry;*

P-0372

ORGANOCATALYSIS OF DYNAMIC IMINE BOND EXCHANGE

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Oganocatalysis by primary and secondary amines via enamine and iminium intermediates has been actively pursued in recent years to facilitate carbonyl condensation reactions.[1] Reversible covalent bond formation and exchange of imines are fundamental reactions in organic chemistry.[2, 3] Recently, the imine bond exchange has been given considerable attention with the development of dynamic covalent chemistry.[2] In this study, we describe the component exchange of imines using L-proline as an organocatalyst to significantly accelerate the exchange reaction, in some cases, up to a 10-fold rate increase.

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Keywords: *Combinatorial chemistry; Organocatalysis; Supramolecular chemistry;*

P-0373

RCM–ELECTROCYCLIC RING OPENING AND RCM-ISOMERIZATION SEQUENCE FOR THE SYNTHESIS OF (Z, E)-DIENOIC ACIDS AND Α,Β-UNSATURATED Δ-VALEROLACTONES

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(*Z*, *E*)-Dienoic acids and their derivates are lead structures in many natural products. The dienoic acid building block is either part of a ring system, e. g. a macrolactone, or in the side chain of the natural product. Examples are the antiviral and cytotoxic macrolactins[1]or the cleorodane diterpenes [2]. α,β-Unsaturated δ-valerolactones are also found in numerous natural products, such as the well known fostriecin.[3]

Both RCM sequences starts with the same starting materials, but the product depends on the use of the chemical trigger.

We developed a new synthetic strategy to (*Z*, *E*) dienoic acids.[4] The key step is a one-pot ring closing metathesis/ base induced rearrangement sequence, which proceeds in high yields and very high (*E*/*Z*)-selectivity.

The key step for the synthesis of δ-lactones is a one-pot ring closing metathesis/ isomerization sequence with triethylsilane as chemical trigger, which proceeds in high yields.[5]

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Keywords: *ring closing metathesis;*

P-0374

PULSED NMR ELUCIDATION OF CURING PROCESS OF EPOXY RESIN

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Introduction: Pulsed NMR method is generally used to elucidate certain aspects of polymer structure and molecular motion. Spin-lattice relaxation time, T_1 and spin-spin relaxation time, T_2 are parameters sensitive to the behavior of molecular motion, such as a chain entanglement or the permanent cross-links of polymers. The curing process of epoxy resin forms a network structure and restricts its chain mobility. We, therefore, applied this method to study a curing process of epoxy resin in terms of mobility of spin.

Method: The same volumes (0.2ml) of epoxy resin and curing agent was mixed in a glass tube (6mmΦ) for 1min and then put into NMR tube (10mmΦ). The reaction was carried out in the probe and then solid echo signals were recorded for T_2. T_1 was obtained by saturation recovery method.

Results and Conclusions: As the curing reaction proceeds, three kinds of T_2(T_{2L}; long,T_{2S}; short,T_{2M}; intermediate) were obtained from the observed solid echo signals. A short T_2(T_{2S}) below 20us suggests an existence of a motion restricted polymer chains, that is, cured element of resin and its fraction (F_S) increased sigmoidally with its reaction time.On the other hand, $F_L$decreased reciprocally against the reaction time, suggesting the disappearance of highly mobile molecules arose from pre-cured resin. F_M showed the behavior of transition between the above two fractions, that is, F_L gives birth to F_S, *via* F_M. The time course of T_1 linearly increased with the reaction, which is reasonably explained by the BBP theory. DSC measurement on the process was also carried out. Heat-flow rate curves against reaction time are parallel to that of F_S, which means that reaction heat is closely related to the appearance of F_S. These results explain that the curing process reflects on the time course of relaxation times and their fractions obtained by pulsed NMR method.

Keywords: *NMR Spectroscopy; Polymerization;*

P-0375

PHOTOSWITCHABLE KINASE INHIBITORS

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Remote-controlling kinase activity is a convenient tool to investigate cell signaling pathways in anticancer research. Photoresponsive kinase inhibitors were designed which can be turned on and off by light of a certain wavelength allowing reversible control of the activity of Erk1/2 kinase in a living cell.

Dithienylethenes (DTEs) are a well-established class of photochromic molecules.[1] By modifying the substituents of the thiophenes, ATP competitive kinase inhibitors were synthesized and their photochromic as well as biological activities were investigated.

Irradiating a methanol solution of all target compounds as ring-open photoisomers with UV light (312 nm) resulted in an immediate conversion to obtain the appropriate ring-closed photoisomers. Upon exposure to visible light ($\lambda > 420$ nm) the reverse process was observed. The ring-closing/-opening cycles could be repeated at least seven times without any major signs of degradation.

OHG cells were treated with the target compounds and their ability to inhibit Erk1/2 kinase activity was evaluated by an ELISA. The regulation of enzyme activity by irradiation with visible and ultraviolet light was confirmed.

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Keywords: *Inhibitors; Isomerization; Medicinal chemistry; Photochemistry;*

P-0376

COVALENT GRAFTING OF BIOCIDAL COPOLYMERS ONTO PVC SURFACES

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Polyvinyl chloride (PVC) is known as a highly versatile polymer with an excellent balance of properties particularly adapted to biomedical devices. In fact, more than 5% of PVC is employed in biomedical applications. However, their applications are limited by the phenomenon of bacterial infection.

In order to overcome this problem, some strategies have been investigated such as antibiotics impregnation of biomaterials or surface modification by grafting bioactive molecules. Within this last strategy grafting bioactive copolymers onto biomaterials surfaces is now considered as a long term option.[1, 2]

In this work, four new biocidal copolymers containing quaternary ammoniums or phosphoniums groups were synthesized, purified and characterized by spectroscopic (FTIR and NMR) and thermal (TGA and DSC) analysis.

Their bactericidal activity was probed against Escherichia Coli (Gram-negative bacteria) and Staphylococcus Epidermidis (Gram-negative bacteria) by evaluating their Minimum Inhibitory Concentration (MIC).

These hydrophilic copolymers were covalently grafted onto PVC-N_3 surfaces using a metal catalyzed azide/alkyne ‘click’ reaction.

The surface modification of the PVC-N_3 was evidenced by contact angle measurements and the surface charge density was evaluated by a fluorimetric method.

At last, the assessment of bactericidal efficiency was performed using the “live and dead” test by fluorescence microscopy.

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Keywords: *polymers; biological activity; click chemistry; Fluorescence;*

P-0377

BORATE ESTER MEDIATED AMIDATION AND TRANSAMIDATION REACTIONS

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The formation of an amide bond is an essential transformation in organic chemistry, the amide bond is found in 25% of known drugs.[1] It is a condensation reaction between a carboxylic acid and an amine with the elimination of one molecule of water. Amidation reactions typically require preactivation of the carboxylic acid as an acid chloride or anhydride, or the use of coupling reagents, which reduces the efficiency of the reaction. We have previously shown that tris-(2,2,2-trifluoroethyl) borate [$B(OCH_2CF_3)_3$] can be used to amidate unactivated carboxylic acids.[2] We have recently developed a cheaper and more convenient procedure for the synthesis of $B(OCH_2CF_3)_3$ from boric anhydride (£27/kg) instead of boron tribromide (£765/kg).[3]

Unlike previous work involving stoichiometric boron reagents for amidation $B(OCH_2CF_3)_3$ does not require anhydrous conditions or an excess of the carboxylic acid or amine for the reaction to proceed efficiently. A wide range of amides can be synthesised containing aliphatic, aromatic and heteroaromatic substituents on both the acid and amine partner.[3] The synthesis of paracetamol has also been carried out using this methodology. The products are purified *via* simple aqueous or solid phase work up. This method is also useful for the amidation of *N*-protected amino acids with both primary and secondary amines.[3] A formylation method using DMF in the presence of $B(OCH_2CF_3)_3$ has also been developed.[3] Trimethoxyboroxine was investigated as an amidation reagent and displayed similar utility to $B(OCH_2CF_3)_3$. We have carried out an NMR study to elucidate the reaction mechanism.

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Keywords: *Amides; Borates; Boron; Carboxylic acids; Amines;*

P-0378

FLUOROALKYLIDENES SYNTHESIS FROM BENZOTHIAZOLYL DERIVATIVES

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The fluorovinylic moiety has been introduced onto several bio-active compounds such as vitamins, prostaglandins, hormones, pheromones and peptide isosteres. However, access to fluoroalkylidenes is not straightforward and required numerous steps including functionalization of fluoroacrylates easily obtained by HWE reaction.

In 2002, our group described the first one step synthesis of fluoroalkylidene *via* the modified Julia reaction. Since this report, our main research deals with the preparation of various alkylated fluorobenzothiazolylsulfones as new building blocks for the expeditive synthesis of fluoroalkenes.

For the preparation of alkylfluorosulfones, our strategy is based on alkylation reactions under Barbier conditions of benzothiazolylsufonyl fluoroacrylate using alkyl iodides and alcohols, followed by a decarboxylation process carried out under Krapcho conditions.

Currently, this approach is applied for on the developement of new peptidomimetics. Indeed, we already reported the expeditive synthesis of fluorinated dipeptide analogues using the modified Julia reaction. Our recent results will be presented.

Keywords: *Julia reaction; fluorine; olefination; Peptidomimetics; alkenes;*

P-0379

THE INFLUENCE OF PERFLUORINATED SUBSTITUENTS ON THE NUCLEOPHILIC REACTIVITY OF SILYL ENOL ETHERS

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Introducing fluorine into organic molecules can alter the properties of these substances substantially, especially concerning their biological activity.[1] Therefore, fluorinated compounds are of interest for pharmaceutical and agricultural industry. Intrigued by their unique properties we have employed the benzhydrylium methodology to investigate the effect of perfluorinated alkyl and aryl groups on the reactivities of silyl enol ethers, which are important building blocks in organic synthesis.[2]

As benzhydrylium ions with variable *p*- and *m*-substituents cover a broad range of reactivity while the steric shielding of the reaction center is kept constant, they have been used as reference electrophiles for the construction of a comprehensive nucleophilicity scale based on eq 1, in which electrophiles are characterized by one parameter (*E*) and nucleophiles are characterized by the solvent-dependent parameters s_N (sensitivity) and *N* (nucleophilicity).[3]

$\log k(20\ °C) = s_N(N + E)$ (1)

We now studied the kinetics of the reactions of fluorinated silyl enol ethers with benzhydrylium ions by UV–Vis spectroscopy in dichloromethane in order to quantify the deactivating effects of perfluorinated groups. Comparison of previously reported nucleophilicity parameters of silyl enol ethers[3] with those of their fluorinated analogues shows that fluorination decreases the nucleophilic reactivity tremendously. Thus, $H_2C{=}C(CF_3)OSiMe_3$ is 10^6 times less reactive than $H_2C{=}C(CH_3)OSiMe_3$ and $H_2C{=}C(C_6F_5)OSiMe_3$ is 10^4 times less reactive than $H_2C{=}C(C_6H_5)OSiMe_3$. These fluorinated enol ethers thus have similar nucleophilicities as ordinary alkenes.3

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Keywords: *Silanes; Substituent effects; Kinetics; Linear free energy relationships; Fluorine;*

P-0380

ESI-MS STUDIES OF OXIDATIVE PALLADO-CATALYZED REACTIONS

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Comprehensive mechanistic investigations usually require kinetic data, identification of catalytic species and a global reaction law. For processes based on combination of different parameters, such as catalytic reactions, the proposition of a mechanism and the selection of the active species for the determination of the rate law may not be accurate. ESI-MS has rapidly become a major tool in identifying reactive intermediates and has achieved great success in mechanistic investigations.[1]

Most of the examples of palladium catalysis consist of nonoxidative methods, especially cross-coupling reactions. Oxidative reactions tend to be more challenging; they require the use of an external oxidant, and the conditions are incompatible with air-sensitive phosphine ligands, which have been critical to the success of the Pd^0-catalysed cross-couplings. As a result, palladium-catalyzed oxidative reactions have received less attention than their nonoxidative counterparts and their mechanisms are less known.

We will present the mechanistic studies developed by ESI-MS in our laboratories over the past years on various pallado-catalyzed reactions.[2] We have for examples shown that dinuclear palladium complexes are more involved as active catalytic intermediates than mononuclear species in the Wacker oxidation of alkenes. A cascade reaction from allylphenols leading to 2-(1,2-dihydroxypropyl)phenol derivatives will be presented. The nature of the catalytic species involved in dehydrogenative Heck reactions and in the formation of diarylalkanes, through C-H activation, will be also discussed.

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Keywords: *Mass spectrometry; C-H activation; Homogeneous catalysis; Reaction mechanisms; Palladium;*

P-0381

ANALYSIS OF THERMAL DEGRADATION BEHAVIORS OF POLYKETONE/POLYAMIDE-6 BLENDS

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An aliphatic polyketone (PK) terpolymer consisting of carbon monoxide, ethylene, and propylene has excellent properties such as low water absorption, superb chemical resistance, low gas permeability, and high heat distortion temperature. Polyketone is well miscible with polyamide-6 due to H-bonding between –C=O in polyketone and –NH- in polyamide-6, and the mechanical properties of polyketone are to be easily controlled through blending with polyamide-6. So the blends are thought to be the promising materials for the automotive parts, especially under the hood. During the residence at the processing temperatures, however, the blends have a chance to degrade easily. The thermal degradation behaviors of the blends with additives were observed. After long time residence for more than 60 min at 250 °C (the upper limit temperature recommended for injection molding of the blends), the initial single melting peak split into two peaks corresponding to polyketone and polyamide-6 moiety, respectively. With increasing content of polyamide-6 in the blends, the melting points of polyketone moiety in the blends showed the tendency of significant decrease with increasing content of polyamide-6 in the blend, but the melting points of polyamide-6 moiety were almost constant. TGA isothermal measurement at 250 °C for 60 min showed the weight reduction was enlarged with increasing content of polyamide-6 in the blends. Inorganic particles were compounded in the blends in order to improve the thermal stability at the processing temperature. With decreasing the size of the particles, the thermal stability of the materials was more improved, especially in tens of nano size. In conclusion, polyamide-6 tends to accelerate the thermal degradation of polyketone in the blends, but polyamide-6 itself will not degrade at high processing temperature. Nano inorganic particles are good additives for the improvement of thermal stability of polyketone and its blends with polyamide-6.

Keywords: *Polymers; Amides; Ketones;*

P-0382

GOLD-CATALYZED SYNTHESIS OF FLUORINATED 2,5-DIHYDROFURANS AND 3,4-DIHYDROPYRANS

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The enormous potential of fluorine-substituted molecules in organic chemistry is reflected in a special interest of new synthetic strategies. Based on the significant change of chemical and physiological properties there exist many pharmaceutical and industrial applications. [1] These include solubility, lipophilicity, metabolic stability and bioavailability by replacement of hydrogen with fluorine.[2–3]

In terms of heterocyclic structures several methods for C-F-bond formation have been developed using electrophilic and nucleophilic fluorination reagents. Examples to form fluorinated precursors as well as fluorination of the heterocyclic products are known.[4–5] Particularly interesting are tandem-fluorination-cyclization reactions using Selectfluor or NFSI (N-Fluorobenzenesulfonmide) as fluorelectrophiles.[6–7]

The gold-catalyzed cycloisomerization of α- and β-hydroxyallenes forming 2,5-dihydrofurans and 3,4-dihydropyrans, respectively, is a well-known reaction. [8] Using this selective formation to prepare fluorinated cycloisomerization products is of particular value for the total synthesis of natural compounds and their derivatives.

In this project, the gold-catalyzed cycloisomerization of α- and β-hydroxyallenes forming fluorinated cyclization products is pursued. First results of our investigations and their perspectives are reported.

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Keywords: *Gold; Allenes; Cyclization; Fluorine; Heterocycles;*

P-0383

ADAPTOMERS: ENHANCING TRANSPORT PROPERTIES THROUGH MOLECULAR ADAPTABILITY

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The bioavailability of an agrochemical or drug molecule at the target site requires the successful balance of physicochemical properties such as aqueous solubility and membrane permeability.[1] Such properties are often inversely related and so designing the optimum molecule generally requires a compromise in one or both properties. An alternative strategy is to design molecules that can adapt their physical properties to match their environment, allowing, for example, simultaneously high aqueous solubility and membrane permeability.[2] The authors present a systematic study into the use of intramolecular hydrogen-bonding as a tool for molecular adaptability in a series of heteroaryl ureas. The relationship between the intramolecular hydrogen-bonding equilibrium constant (K_i) and a number of measured and calculated physicochemical properties will be discussed.

P-0384

A HIGHLY SELECTIVE DIARYLPROLINOL SILYL ETHER CATALYST IMMOBILIZED ON PHOSPHOROUS DENDRIMERS AND MAGNETIC NANOBEADS

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Over the last years the immobilization of catalysts on solid supports became of increasing interest with regard to recycling and protection of environmental resources. [1] The choice of the support mainly depends on its physical, thermal and chemical stabilities. Furthermore, the decision is also dependent on the ease of recovery of the supported catalyst. Classic heterogeneous catalysts were recovered by filtration or extraction techniques, however, they often suffer from the drawback of a low activity in comparison to homogeneous catalysts. In contrast, semi-heterogeneous catalysts combine the benefits of heterogeneous and homogeneous catalysis by linking a homogeneous catalyst to readily dispersible nanoparticles [2] or soluble macromolecules (e.g. polymers, PEG or dendritic structures) [3] which can be precipitated at the end of the reaction.

Here, we report the immobilization of a diarylprolinol silyl ether catalyst on phosphorous dendrimers and polymer-coated magnetic nanobeads as semi-heterogeneous spherical supports. The catalysts were successfully used in the enantioselective Michael addition of propanal to (*E*)-b-nitrostyrene. The reactions showed good to excellent yields, diastereoselectivities and enantioselectivities. Furthermore, a positive dendritic effect was observed. Recycling was achieved by precipitation and filtration in the case of dendrimers and magnetic decantation in the case of magnetic nanobeads.

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Keywords: *Michael addition; Nanoparticles; Dendrimers;*

P-0385

CHEMOSELECTIVE CROSS-COUPLING REACTIONS WITH DIFFERENTIATION BETWEEN TWO NUCLEOPHILIC SITES ON A SINGLE THIOPHENE BUILDING BLOCK

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Transition metal catalyzed cross-coupling reactions are among the most powerful tools in synthesis.[1] In contrast to the well-established electrophile-selective cross-coupling reactions, nucleophile-selective cross-coupling reactions are barely described in synthetic organic chemistry. We have systematically developed a nucleophile-selective cross-coupling method with excellent isolated yields, using the different reactivities of the Stille reaction and Suzuki-Miyaura cross-coupling reaction.[2] For this purpose, we synthesized a thiophene building block, bearing a stannyl group and boronic ester in 2- and 5-position, which can undergo a selective Stille coupling with a wide range of electrophiles. The remaining boronic ester can be used for a separate Suzuki coupling, which may be performed in an efficient one-pot approach.

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Keywords: *Cross-coupling; Chemoselectivity; Heterocycles; Homogeneous catalysis;*

P-0386

EFFECTS OF THE NANO ZNO POWDER IN SOME THERMAL AND PHYSICAL PROPERTY OF RIGID POLYURETHANE FOAMS

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Development of rigid polyurethane foams (RPUF) in the industrial insulation, and saving energy was cased the importance of thermal conductivity and isolation property of RPUF. The properties of rigid polyurethane foams can be modified over a wide range depending on the raw materials used for its synthesis. The objective of this study is to investigate an appropriate process to fabricate the polyurethane Nanocomposites. In nanocomposites, nano powders were used as nucleating agent to decrease a cell size of the RPUFs as well as improve the thermal insulating properties of rigid polyurethane foams. Rigid polyurethane foams Nanocomposites (R PUFs) that contain up to 0.93% Zinc oxid were successfully fabricated from polymeric 4,4-diphenylmethane diisocyanate, polyether polyols, nano ZnO powder, silicone surfactant, hydrochlorofluorocarbon (HCFC) 141B, and distilled water. This Nanocomposite 30% decreased amount of thermal conductivity in 0.93% (w/w) Zinc oxid than reference.

Keywords: *rigid polyurethane foam; thermal conductivity; Nanocomposit; Nucleating agents; ZnO;*

P-0387

ATROPISOMERIC CHIRAL 4,4'-BIPYRIDINES

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4,4'-Bipyridine is one of the most famous ligand used in supramolecular chemistry due to the presence of two donor atoms along a rigid structure. Considering the importance of chiral supramolecular networks in many applications such as asymmetric catalysis, it was surprising to find limited examples of chiral 4,4'-bipyridines in the literature. Based on our recent synthesis of polyhalogenated 4,4'-bipyridines [1], we report herein two methods for the preparation of enantiomerically pure 4,4'-bipyridines. The first method is based on the synthesis of a chiral tetrahalogenated 4,4'-bipyridine (substituted in 3,3',5,5') which after selective cross-couplings yields several atropisomeric derivatives. The enantiomers are separated by chiral HPLC and their absolute configurations are determined by X-ray diffraction (XRD) and electronic circular dichroism (ECD). Alternatively, the chiral tetrahalogenated 4,4'-bipyridine can be first enantioseparated and then involved in cross-coupling reactions without racemization [2, 3]. The second method concerns the direct functionalization in 3-position of an achiral tetrahalogenated 4,4'-bipyridine (substituted in 2,2',5,5') to generate atropisomeric chiral 4,4'-bipyridines; this second method allows for asymmetric synthesis. Chiral HPLC allows easy enantioseparation due to a butressing effect of substituent in 2-position [3] and the absolute configurations of the separated atropisomers are determined by XRD and ECD. In order to show the potential interest of these new chiral ligands for Metal Organic Frameworks (MOFs) synthesis and applications, some metal complexes including tetrahalogenated 4,4'-bipyridines and derivatives will be presented.

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Keywords: *Atropisomerism; Biaryls; Circular dichroism; Configuration determination; Chiral resolution;*

P-0388

HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY ENANTIOSEPARATION OF ATROPISOMERIC 4,4'-BIPYRIDINES ON IMMOBILIZED POLYSACCHARIDE-BASED CHIRALPAK IA AND CHIRALPAK IC: IMPACT OF SUBSTITUENTS AND ELECTRONIC PROPERTIES

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More than other techniques [1], high-performance liquid chromatography (HPLC) on chiral stationary phases (CSPs) is the most used for the enantioseparation of chiral compounds. Recently, this technique has been successfully applied to the preparation of pure enantiomers of new atropisomeric 4,4'-bipyridines [2–3]. Due to the novelty of the field, asymmetric procedures devoted to the preparation of optically pure 4,4'-bipyridines are not available yet in the literature. The 4,4'-bipyridyl system is one of the most used connectors between transition metal atoms for building metal organic frameworks (MOFs) due to its structural and topological characteristics. Chiral MOFs are of great interest in asymmetric catalysis and the access to enantiopure 4,4'-bipyridines is therefore highly required. Based on the chromatographic methods recently developed by us for the enantioseparation of atropisomeric 4,4'-bipyridines by using coated polysaccharide-based CSPs [4], we report herein new and efficient methods for the direct enantioseparation of 3,3',5,5'-tetrahalogenated, 2,2',3,3',5-pentahalogenated, 3,3'-dibromo-5,5'-disubstituted and 2,2',3,3'-tetrahalo-5-substituted 4,4'-bipyridines on two immobilized polysaccharide-based CSPs, Chiralpak IA and Chiralpak IC. The impact of structural modifications inside the bipyridyl skeleton on the separation behavior was investigated through a parallel evaluation of experimental data, such as retention (k) and separation factors (α), resolution (R_s) and density functional theory (DFT) computed molecular properties of the analytes. The semipreparative recoveries of optically pure atropisomers of the examined 4,4'-bipyridines provide valuable starting materials for the future preparation of homochiral MOFs.

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Keywords: *Biaryls; Molecular recognition; Enantioselectivity; Analytical Methods; Atropisomerism;*

P-0389

SYNTHESIS OF ANALOGUES OF AZT WITH TRIAZOLE MOIETY

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Currently**, AIDS** (Acquired Immune Deficiency Syndrome) is considered as a pandemic, causing about 1.8 million deaths between 1981 (date on which the first case of AIDS was identified) and 2009**. AZT** or 3'-azido-3'-deoxythymidine was the first antiretroviral approved for the treatment of AIDS. This compound, due to the absence of the hydroxyl group in position 3', inhibits reverse transcriptase, and prevents the extension of the viral DNA chain and finally viral replication of the RNA.

Herpes is a viral disease caused by both Herpes Simplex Virus type 1 (HSV-1) and type 2 (HSV-2). This pathogen, in its various forms, affects more than 90% of the population worldwide. Acyclovir or 9-[{2-hydroxyethoxy}-methyl]-guanosine (ACV) is an acyclic analogue of the natural nucleoside 2'-deoxyguanosine, considered as the first choice of treatment for herpes simplex virus types 1 and 2. ACV is also deprived of this 3'-OH function present in the natural nucleosides, inhibits herpes DNA polymerase, and behaves as a "suicide inhibitor"

As part of the discovery of new molecules to complete the therapeutic arsenal directed to these two viral diseases, we are interested in the synthesis of a new family of antiretroviral of the AZT type with a 1,2,3-triazole-1,4-disubstituted moiety. These compounds were tested against HIV in collaboration with the group of Professor Raymond F. Schinazi (Emory University School of Medecine/Veterans Affair Medical Center, Atlanta, Georgia 30033, USA) and against herpes in collaboration with Professor Nathalie Bourgougnon (University of Bretagne Sud, Laboratory of Biotechnology and Marine Chemistry, Vannes).

Keywords: *Click Chemistry; Drug discovery;*

P-0390

TRIBENZOTRIQUINACENE – A NEW AND VERSATILE SYNTHESIS

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Tribenzotriquinacene is a rigid bowl-shaped hydrocarbon that was first synthesized by Kuck and co-workers. We have developed a new synthesis of this intriguing molecule which affords the parent compound in higher yield. In addition, our synthetic scheme allows easy preparation of *ortho*-functionalized and C_3-chiral derivatives that have so far only been poorly accessible. These derivatives are interesting for asymmetric catalysis and supramolecular chemistry and their chiral resolution by HPLC is reported.

Keywords: *hydrocarbon chemistry; bowl-shaped molecules; chiral resolution;*

P-0391

QUANTITATIVE PREPARATION OF 3,4-DI(METHYLENE)TETRAHYDROTHIOPHENE-1,1-DIOXIDE BY ZN-INDUCED 1,4-ELIMINATION. A 6-C SYNTHON FOR THE PREPARATION OF A SHORT-CHAIN [4+2] C60 MONOADDUCT.

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Our interest in the synthesis of [60]fullerene derivatives derived from the Diels-Alder reaction in combination with the limitations posed by the current methods which utilize 2,2'-bisallyl-diradical prompted us to investigate the optimum reaction conditions for the preparation of 3,4-di(methylene)tetrahydrothiophene-1,1-dioxide and the subsequent efficient synthesis of a short-chain [4+2] C_{60} monoadduct bearing a reactive site for further functionalization.

In summary, we have demonstrated a practical and efficient preparation of the highly reactive 3,4-di(methylene)tetrahydrothiophene-1,1-dioxide. Optimization of the reaction parameters allow the quantitative preparation of the diene-sulfone *via* a zinc-induced 1,4-elimination of 3,4-bis(bromomethyl)-2,5-dihydrothiophene-1,1-dioxide with no signs of polymerization. In particular, acetone was the solvent of choice at a concentration of 6 mg/mL. Activated Zn-dust promoted efficiently the 1,4-elimination step while, the shortest reaction time was achieved with microwave irradiation. The diene-sulfone can be employed in Diels–Alder reactions with dienophiles either in acetone or after exchanging the solvent with dry benzene where the diene remains stable for several weeks at -20 °C. The overall yield of the one-pot procedure (1,4-elimination/Diels-Alder reaction) when DMAD was utilized as a dienophile was more than 90%. Zinc incompatible dienophiles can be treated with acetone solutions of diene-sulfone by simply filtration of the zinc salts prior to the Diels-Alder cycloaddition. The diene-sulfone synthesized under the aforementioned optimum conditions was utilized for the synthesis of a [4+2] C_{60} monoadduct bearing a masked-diene moiety. The applied method led to the successful preparation of the C_{60} cycloadduct isolated in 56% yield.[1]

Dienophiles with a wide range of chemical functionalities could be employed to provide a novel post-synthetic modification strategy *via* cheletropic extrusion of SO_2 targeting novel C_{60} derivatives for various applications in materials science.

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Keywords: *3,4-di(methylene)tetrahydrothiophene-1,1-dioxide; [60]fullerene; [4+2] monoadducts; six carbon (6-C) synthon; 2,2'-bisallyl diradical; chemoselective one-pot 1,4-elimination/[4+2] cycloaddition/aromatization;*

P-0392

SYNTHESIS AND STRUCTURAL ELUCIDATION OF NOVEL 2-[(1E,3E)-4-ARYLBUTA-1,3-DIENYL]QUINOLIN-4(1H)-ONES

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Quinolin-4(1*H*)-ones are well known heterocyclic compounds due to their significant biological properties. A wide variety of clinical applications have been approved for these compounds including the treatment of respiratory, gastrointestinal, and gynaecologic infections, sexually transmitted diseases, prostatitis and some skin, bone and tissues infections.[1] Quinolin-4(1*H*)-ones are a class of drugs that target the bacterial type II DNA topoisomerases and could also inhibit mammalian topoisomerase activity and tubulin polymerization thus acting as potent antitumor agents.[2] They are also cytotoxic agents and cardiovascular protectors.[3, 4]

Following our previous studies on (*E*)-2-styrylquinolin-4(1*H*)-ones,[5,6] now we report the synthesis of their highly conjugated analogues 2-[(1*E*,3*E*)-4-arylbuta-1,3-dienyl]quinolin-4(1*H*)-ones, which are very important scaffolds for the synthesis of new 1-arylacridin-9(10*H*)-ones. The developed synthetic methodology involves the condensation of 2'-aminoacetophenone with (2*E*,4*E*)-5-arylpenta-2,4-dienoic acid derivatives in the presence of DCC and 4-pyrrolidino-pyridine to give the (2*E*,4*E*)-*N*-(2-acetylphenyl)-5-arylpenta-2,4-dienamides in moderate yields. Finally the base-induced cyclization of these dienamides afforded the desired 2-[(1*E*,3*E*)-4-arylbuta-1,3-dienyl]quinolin-4(1*H*)-ones in good yields. To the best of our knowledge, the synthesis of these quinolin-4(1*H*)-ones or their *N*-substituted derivatives is not reported as well as their structural elucidation which was accomplished by 1D and 2D NMR spectroscopic studies.

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Keywords: *Nitrogen heterocycles; Conjugation; Alkylation; Cyclization; NMR spectroscopy;*

P-0393

POLYMER BLENDING AS MACROSCOPIC EXPRESSION OF MOLECULAR RECOGNITION

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Polymer blends are widespread materials used in modern industry and represent one of the most rapidly growing areas in polymer science.[1] Numerous attempts have been made to minimize interfacial energy and reduce the propensity for phase segregation of the polymers. One of the most appealing approaches has been the use of non covalent interactions such as hydrogen bonding.[2] Recently, our research group has developed tetraphosphonate cavitands as monomers for supramolecular polymers. They present outstanding molecular recognition properties towards positively charged species such as N-methylammonium and N-methylpyridinium moieties.[3] Herein we present our recent results on molecular level mixing of two immiscible polymers, such as polystyrene (PS) and poly(butyl)methacrylate (PBMA),[4] through host-guest interactions. Specifically, we embedded a tetraphosphonate cavitand along the backbone of PS as host (PS-Host) and a N-methylpyridinium derivative in the skeleton of PBMA as guest motif (PBMA-Guest). The formation of a supramolecular polymer architecture was demonstrated in solution by ^{31}P-NMR and in solid state by atomic force microscopy and differential scanning calorimetry. The AFM image of 50% PS-Host:50% PBMA-Guest mixture shows no phase separation in accordance with the formation of supramolecular network. A DSC study of the blend shows a single T_g at temperature intermediate between the T_g of the two starting polymers. Moreover chemically induced segregation has been triggered by addition of a competitive guest (N-methylbutylammonium chloride) which replaced the N-methylpyridinium moiety in cavitand binding.

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Keywords: *Host-guest systems; Polymers; Supramolecular chemistry; Molecular recognition; Cavitands;*

P-0394

SYNTHESIS OF MOLECULES FOR THE CONTROLLED FUNCTIONALIZATION OF GRAPHENE SURFACES

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Graphene, a monolayer of carbon atoms packed in a two-dimensional honeycomb lattice, has lately become a very interesting material, being endowed with exceptional physical properties.[1] In particular, electronic properties constitute one of the most investigated aspects of graphene, which is considered a zero band gap semiconductor. Chemical functionalization represents a promising approach for opening a band gap into its energetic levels, but, if many ways have been suggested to functionalize the surface in a non-covalent[2] or covalent[3] "random" fashion, controlled functionalization (i. e. only at selected sites) has not yet been described. The innovative approach we suggest to get precise control on the sites of chemisorption of the molecules is to switch from "chemistry in solution" to "on-surface chemistry": it has been envisaged to design molecules self-organizing on graphene surfaces and control their chemisorption at an atomic scale precision resorting to STM techniques. Here we present the synthesis of molecules characterized by the presence of groups potentially reactive under the STM tip and long alkyl chains to enlarge the stability of the assemblies[4] and allow a control of their geometry[3a], as well as the first results of the STM studies.

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Keywords: *Scanning probe microscopy; graphene; Supramolecular chemistry;*

P-0395

APPLICATIONS OF HYPERVALENT IODINE REAGENTS IN THE PREPARATION OF SYNTHETIC QUINOIDS

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Naturally occurring quinones and quinols are very interesting chemical leads with several biological activities[1]. To prepare these promising compounds a number of procedures were found in the literature[2], but all of them have some restrictions.

As part of a program directed at the discovery of new antiprotozoal agents, we were interested in the facile construction of the *p*-quinol skeleton. Hypervalent iodine reagents (phenyliodine(III) diacetate, phenyliodine(III) bis-trifluoroacetate, etc.) are a versatile oxidation tool meeting the concept of green chemistry because of their low toxicity, easy handling, safety and ready availability[3].

Here we report a practical and general method to prepare a series of quinol-derivatives using hypervalent iodine reagents. Commercial available *para*-substituted phenols and their briefly modified derivatives acted as starting material.

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Keywords: *Hypervalent iodine; dearomatization; p-quinol; antiprotozoal;*

P-0396

HIGHLY DIASTEREOSELECTIVE METHOD FOR THE PREPARATION OF 1,2-ALKENYL DIOLS

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The development of new and highly diastereoselective processes for the creation of carbon-carbon and carbon-heteroatom bonds is one of the major targets in chemical synthesis. In contrast to tertiary stereocenters, the construction of quaternary stereocenters, that are carbon centers bearing four different non-hydrogen substituents, represents one of the most challenging and dynamic areas in organic synthesis. The state-of-the-art is the asymmetric construction of such quaternary stereocenters in non-cyclic systems (more complicated due to the number of degrees of freedom associated with these structures). Most of the current methods produce only one carbon-carbon bond per chemical step and, therefore, may suffer from low efficiency. Recently, we have developed highly diastereoselective and efficient process for the construction of 1,2-alkenyl diol moiety from simple alkynyl ethers through the formation of several carbon-carbon bonds in one chemical step (T. Mejuch, M. Botoshansky, I. Marek, *Org. Lett.* **2011**, *13*, 3604; T. Mejuch, B. Dutta, M. Botoshansky, I. Marek, *Org. Biomol. Chem.* **2012**, Advance Article **doi:** 10.1039/C2OB25121C). The stereochemistry was rationalized through a Zimmerman-Traxler transition state, in which the bulky group of the carbonyl occupies a pseudo-axial position to avoid one gauche interaction (N. Gilboa, H. Wang, K. H. Houk, I. Marek, *Chem. Eur. J.* 2011, *17*, 8000).

Keywords: *allylation; carbonyl compounds; diastereoselective synthesis;*

P-0397

SYNTHESIS OF NANO-CLIP AND NANO-BOX COMPOUNDS HAVING FREE BASE PORPHYRINS AS WALL

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There is interest in developing smart nanostructures for applications in many different fields, from environmental monitoring to biological, medical and industrial chemistry. For some specific properties, porphyrin-derivatives are among the most studied compounds and some applications like chemical and/or biological receptors, artificial sensors for drug determinations, mimesis of biological systems, etc., are already well-defined. Recently, several 3D cyclic oligo-porphyrins with different architectures have been studied. The properties of these molecules may depend on the size and the hydrophobic nature of cavities inside their 3D structure (e.g. suitable to accommodate hydrophobic chemicals).

In this work, the synthesis and characterization of some novel water soluble macromolecular cyclic ethers, constituted by two or four porphyrin units and spaced with methylene bridges, are reported. These compounds, obtained by reaction between dibromomethane and 5,15-di[p-(9-methoxytriethylenenoxy)phenyl]-10,20-di[p-hydroxyphenyl] porphyrin, have a co-facial (nano-clip) or a four wall-box (nano-box) architecture.

The aim of these syntheses was to obtain molecular systems for recognition and/or carriage of bio-molecules. In particular, UV-vis titration showed the easy and reversible protonation of the pyrrolic cores with modification of the spatial distance between the two co-facial porphyrins and, therefore, the cavity size. This reversible modification could be used to change dimer molecule status from Open to Closed, and facilitate the accommodation or release of suitable chemical species, acting then as a drug carrier.

Tetrameric porphyrin molecule (a Nano-box) could also be used as a drug-carrier, forming inclusion complexes with macromolecular drugs or as a nano-reactor for the peculiar conditions inside the box. In this last case, 1H-NMR spectroscopic analysis showed a high-field shift of aromatic and ether protons present in the upper and lower box rims as a specific characteristic of this molecular structure. These compounds differ from previous analogous porphyrinic systems in their totally covalent structure that makes them more versatile potential macromolecular tools.

Keywords: *Porphyrinoids; Synthesis design; UV/Vis spectroscopy; NMR spectroscopy;*

P-0398

GRAFTING C_{60}-FULLERENE ON AMINO ACID SIDE CHAIN USING PHOSPHINE BORANE: NEW METHOD AND ELECTROCHEMICAL BEHAVIOR

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Recently, amino acid fullerene derivatives received growing interest in biological field,[1] for their inhibition properties of the hepatitis C virus RP and human immunodeficiency virus-RT.[2] Moreover, these unusual amino acids could be used as markers, due to the specific spectroscopic and electrochemical properties involving the fullerene moiety.[3]

Recently, we synthesized the first amino acid derivatives bearing a secondary phosphine borane, starting from L-aspartic acid. Here, we reported the use of these amino acid derivatives to link the C_{60}-fullerene by P-C bond formation, under phase transfer conditions. The electrochemical behavior of these new fullerene amino acids is described.

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Keywords: *amino acids; fullerene; phosphine borane;*

P-0399

SYNTHESIS OF 4H-CHROMENE DERIVATIVES BY REACTION BETWEEN ALKYL ISOCYANIDES AND DIALKYL ACETYLENEDICARBOXYLATE IN THE PRESENCE OF 7-HYDROXYCUMARINE

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Chromenes constitute a major class of naturally occurring compounds, and interest in their chemistry continues unabated because of their usefulness as biologically active agents. Substituted 4H-chromenes are a new class of anti-cancer compounds. 2-amino-4Hchromenes have been of interest because of their biological activity and some methods have been reported for their synthesis. We now report an efficient synthetic route to 2-amino-4H-chromenes using alkyl isocyanides and dialkyl acetylenedicarboxylate in the presence of 7-hydroxycumarine. The structures were deduced from IR, ^{1}H NMR, ^{13}C NMR spectra.

The present method carries the advantage that not only is the reaction performed under neutral conditions, but also the starting materials and reagents can be mixed without any activation or modification..

Keywords: *2-amino-4H-chromene; 7-hydroxycumarine; alkyl isocyanides;*

P-0400

TOWARDS THE DEVELOPMENT OF SUSTAINABLE P-CONJUGATED MATERIALS: SYNTHESIS OF NEW DONOR-ACCEPTOR SYSTEMS BASED ON EXTENDED BENZODIFURAN DERIVATIVES

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New materials are required to meet the stringent requirements of new generation of consumer electronics such as cell phone displays, computer and television screens, and solar cells. The synthetic pathways of organic semiconductors (OSC) are mainly based on coupling reactions involving metal catalysts. The electronic properties of these materials are strongly dependent on their purity and they must be extensively purified prior to being used in an electronic device. A new challenge for the development of OSC is to target materials that: **1**) are easily prepared, **2**) do not need to be purified, and **3**) have tunable properties.

The project aims to develop new conjugated systems that are compatible for developing organic electronic devices, by using green chemistry processes as condensation reactions which give only water as byproduct during different stages of the syntheses.

In this context we have developed a new series of donor-acceptor materials based on benzodifuran units. The rational of this design relies on the easy access to diamino-benzodifuran derivative bearing a pentafluorophenyl group by condensation of 1,4-benzoquinone with pentafluorophenylacetonitrile. Then, the lengthening of the conjugation was performed by azomethine bonds (isoelectronic of ethylenic bond) obtained by reaction of the diamino compound with aldehyde derivatives carrying short oligothiophene units. Synthesis, electronic properties and the first examples of electronic devices will be discussed; the role of the pentafluorophenyl groups on the supramolecular organization will be also evidenced.

Keywords: *diamino-benzodifuran; semiconductors; green chemistry; devices; azomethine;*

P-0401

CHIRAL BIFUNCTIONAL CATALYSTS BASEDM ON C(SP3)-METALATED PINCER COMPLEXES

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Cooperating ligands are non-innocent ligands that actively participate in reversible structural transformations of catalytic species over the course of a catalytic cycle. The ligand-metal cooperation often brings about unusual and exciting reactivity and plays very important role in natural and artificial systems. Among others, this concept is of great interest for the design of new catalytic bond-breaking/-forming processes, as it offers a non-oxidative mechanistic alternative to the classical oxidative addition/reductive elimination sequence.

Recently [1], we describe the design and synthesis of a new bifunctional dibenzobarrelene-based PC(sp3)P pincer ligand, and its excellent performance in acceptorless dehydrogenation of alcohols. The mechanism of the reaction involving intramolecular cooperation between the structurally remote functionality and the metal center originates from a unique topology of the barrelene-based PC(sp3)Ps.

We wish now to describe the synthesis of new **chiral** nonracemic dibenzobarrelene based PC(sp^3)P pincer ligand.

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P-0402

COLLOID-CHEMICAL APPROACHES TO CRUDE OIL PREPARATION

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Formation of emulsion at an oil recovery is one of the basic problems of a petroleum industry which lead to large oil losses at preparation for processing. Therefore there is a necessity of the decision of the important practical problems, such as clearing of oil from salts and waters which is reached by use of various deemulgators.

Researches of colloid-chemical properties of polyacrylonitrile derivatives compositions with surfactants have allowed to predict their application as deemulgators. Results of researches have shown, that deemulsifier action of polymeric compositions substantially depends on the macromolecules conformation condition defined by a degree of polymer functional groups ionization. It is established, that deemulgation depends also on superficial activation of polyelectrolits compositions with surfactants on the interface.

From the calculated values of superficial activity of polyacrylonitril derivatives compositions with sodium salts of oleic acid follows, that formation of a composition leads to increase in superficial activity and reduction of standard free energy of polymers adsorption.

Increase of ?? with growth of polymer concentration in a mix testifies about interaction between sodium salts of oleic acid with polymers by hydrogen communications formation that leads to change of macromolecules adsorbtion parameters in mixes. In result occurs the shielding of SAS and polymer polar groups, that will lead to increase of macromolecules hydrophobility and strengthening of intra-and intermacromolecular hydrophobic interactions in compositions. Reduction of standard free energy of macromolecules adsorption during of complex formation testifies about macromolecules hydrophobization during formation of the compositions, leading to increase in their superficial activity and ability to adsorbtion on border of phases section.

It is established, that at $n = 0{,}25$ the deemulsifier action of polymeric composition is shown most full, that is explained by conformation condition, influencing on surface activity.

Keywords: *Polyacrilonitrile derivatives; Surfactants; Deemulgation; adsorption; conformation condition;*

P-0403

SYNTHESIS OF 1-METHYL-3,5-DINITRO-1,2,4--TRIAZOLE(DNMT) USING MICROREACTOR

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1-methyl-3,5-dinitro-1,2,4-triazole(DNMT) has excellent IM(Insensitive munitions) capabilities and is used in gas-generating agents. DNMT can be synthesized by nitration of a nitrate salt of 1-methylguanazole(DAMT) with nitrating agents(H_2SO_4 and $NaNO_2$). Attempting to scale up in an usual batch method, we assume that the reaction efficiency is decreased, due to emission of NOx which is a possible nitro source in large quantities out of the system. Therefore we constructed a consecutive reaction process to react NOx efficiently by means of microreactors. In order to establish a reaction process that can accommodate a wide range of compounds, we also studied nitration of DAMT under neutral conditions with Nafion, known as a solid superacid, instead of sulfuric acid.

Keywords: *Microreactors; Nitrogen heterocycles;*

P-0404

COLD PULPING OF BAGASSE

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Amongst the common non-wood fibers, bagasse pulp mills are typically one of the largest non-wood mills which have been built because large volumes of bagasse are available in one spot – the sugar mill. Typically, bagasse pulp is produced in integrated pulp and paper mills, and softwood kraft or sulfite pulp is added to provide the strength requirements to the paper. However, non-wood pulp in particular may be used instead of softwood kraft or sulfite pulp, thus producing a 100% non-wood paper. Since chemical pulping is a high- temperature (~170°C) heat energy intensive process**,** bagasse was cooked in this study in polyethylene bags regarded as containers at 75 °C to produce bagasse pulp. The pulping was carried out in two stages, pretreatment by hot water at 100 °C for 1 hour and chemical pulp by NaOH for 3,4,5 hours. Active alkali charge was 20% based on pre-extracted raw material. Increasing the time of pulping to 5 hours has no effect on pulp yield. In general, beating time of the produced pulp was long. This pulp was characterized by good yield, low tensile strength but high tear strength (1, 2). The mechanical strengths of pulp were improved by adding a blend of starch and borax (1:1) to the pulp before making paper sheets

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Keywords: *Carbohydrates; mechanical properties; Industrial Chemistry;*

P-0405

HETEROGENEOUS ORGANOCATALYTIC SYSTEMS AND THEIR APPLICATIONS

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In the last decade, organocatalysis has emerged as an attractive new field in catalysis[1]. Many organocatalysts were developed and applied specifically in asymmetric organic transformations. However, in order to have efficient organocatalytic reactions, there is a crucial requirement for applying high loading of catalysts; therefore complicated procedures for the isolation of the desired products are needed. In order to cope and minimize such difficulties, a great deal of attention has been invested in developing methods for the heterogenization of homogeneous organocatalysts. In our research, we focus on developing new heterogeneous catalytic systems based on encapsulation of organocatalysts in the cores of chiral and achiral poly-urea microcapsules. Such systems are prepared by emulsification of the organocatalyst in water or apolar organic solvents followed by interfacial polymerization of isocyanate monomers with diamines in O/O and W/O emulsions. Applications of the heterogenized catalytic systems in Michael addition reactions will be shown and the effect of the shell type on the catalytic performance of the encapsulated organocatalyst in asymmetric transformations will be presented.

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Keywords: *Organocatalysis; Heterogeneous catalysis; Chirality;*

P-0406

SYNTHESIS OF NOVEL POTENTIAL ANTITUBERCULOTICS BASED ON 5-SUBSTITUTED BENZYLSULFANYL HETEROAROMATES

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Tuberculosis (TBC) is a widespread infectious disease. About one third of world population is infected with TBC. About 8.8 mil new cases of TBC were found and 1.7 mil people died in 2010. Another major problem is the presence of strains resistant to the conventional treatment. Therefore, the search for new antitubercular drugs, active also against these resistant strains, is highly important.

A lot of works dealing with the synthesis of new antitubercular drugs have been published to date. Many substances were prepared and evaluated, but in fact no one was implemented to the clinical practice. Nevertheless it was discovered that some substances containing benzylsulfanyl group bound on the heteroaromates (benzoxazole, benzothiazole, benzimidazole) had the same or comparable activity as standard isoniazide. Also it was found that antitubercular activity was increased by the addition of electron-withdrawing substituents to the benzylsulfanyl moiety. These substances seem to be perspective and it is necessary to carry out more structure-activity relationship studies.

In our work, the methylenesulfanyl linker between substituted phenyl group and heteroaromates has been modified. Selected compounds with methylenesulfanyl, methyleneoxy and sulfanyl linker and one type without linker were synthesized.

Antimycobacterial activity of these compounds as well as their cytotoxicity on the isolated hepatocytes will be evaluated.

Acknowledgement: *This project was supported by the Grant Agency of Charles University (Project no. 55610/2010) and by the Charles University in Prague (SVV 265 001)*

Keywords: *Medicinal chemistry; Heterocycles; Antibiotics;*

P-0407

INVESTIGATION OF DIFFERENT ORGANIC REACTIONS CATALYSED BY METALS ON HETEROGENEOUS SUPPORTS

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In the last decades one of the main targets of the organic chemical research is to find new catalysts, which are more active, more selective, reusable, can be treated simply, and are environmentally more friendly than the most common catalysts. In the last years the use of different mineral based catalysts became more and more important. Also, these substance are often used as support of different metal catalysts.

At the Department of Organic Chemistry and Technology of BUTE experiments have been made for the use of solid acids and bases in organic syntheses since years. Joining in this research group, my first task was to investigate the applicability of palladium on magnesium-lanthanum mixed oxide support, developed in the group earlier, as catalyst in dehalogenation of aromatic halogenides.

I investigated the reaction with aryl iodides in the presence of sodium hydroxide in ethanol. In most cases I obtained the desired products with acceptable yields. In the case of halonitrobenzenes, in ethanol, in the presence of sodium hydroxide we observed the reduction of the nitro group. Further investigation of this reduction verified a transfer hydrogenation mechanism, the solvent alcohol oxidised to the corresponding acid. Changing the support and the reaction conditions we could also prepare the intermediates (azoxybenzene, azobenzene) selectively, in an environmentally friendly way.

Earlier this palladium catalyst were used succesfully in the Heck-, Sonogashira- and Suzuki-coupling. I examined the possibility of replacing this catalyst with newly improved supported palladium catalysts. The examined model reaction was the Heck-coupling of iodobenzene and styrene.

Based on earlier results of the research group, we also investigated the use of copper on 4A molecular sieve support in the coupling reaction between aryl halogenides and ethyl acetoacetate. Only aryl iodides gave results, under the applied reaction conditions aryl bromides did not react.

Keywords: *Heterogeneous catalysis; palladium; copper;*

P-0408

THE EFFECTS OF APROTIC SOLVENTS AND STRUCTURE ON THE ELECTRONIC ABSORPTION SPECTRA OF THE ISOMERIC PYRIDINE CARBOXYLIC ACIDS

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The ultraviolet absorption spectra of the carboxyl group of three isomeric pyridine carboxylic acids (picolinic acid, nicotinic acid and isonicotinic acid) were determined in a set of aprotic solvents in the wavelength range from 200 to 400 nm. In order to to analyze the aprotic solvent effect on the obtained absorption maxima, the ultraviolet absorption frequencies of the electronic transitions in the carboxylic group of the examined acids were correlated using a total solvatochromic equation of the form $\nu_{max} = \nu_0 + s\pi^* + b\beta$, where ν_{max} is the absorption frequency ($1/\lambda_{max}$), π^* is a measure of the solvent polarity and β represents the scale of solvent hydrogen bond acceptor basicities, the property characteristic for aprotic solvents. The correlation of the spectroscopic data was carried out by means of multiple linear regression analysis. The solvent effects on the ultraviolet absorption maximums of the examined acids were discussed.

Keywords: *picolinic acid; nicotinic acid; isonicotinic acid; ultraviolet absorption maximum; aprotic solvents;*

P-0409

HETEROAROMATIC-STEROID CONJUGATES

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Bile acids are important natural substances that are final products of cholesterol metabolism. They are characterised by typically amphiphilic structure and due to a very special combination of both hydrophilic and hydrophobic side they could be used as lipid emulsifiers or surfactants [1]. Biologically, they have many different biological functions in human body [2, 3].

Aromatic compounds with heterocyclic electro-donors atoms can be used for metal complexations [4]. Firstly, we aimed to preparation of different heterocyclic mono- and di-amines. Next step was reaction of those heterocycles with bile acids giving steroid-aromatic compounds. In dependence on excess of activated acid in reaction with di-amine we observed mono or bisubstitution

For those compounds we expected some self-stacking potential-for that UV/VIS spectra were measured. Also *in-vitro* biological activity tests were done for chosen substrates.

Acknowledgment: *This work was supported by MSM6046137305 (MSMT).*

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Keywords: *steroid; bile acid; heterocycles; UV measurements;*

P-0410

SELECTIVITY CONTROL OF ALKYNE [2+2+2] CYCLOADDITION REACTION AND ITS APPLICATION TO CHAIN-GROWTH CYCLOADDITION POLYMERIZATION REACTIONS

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We demonstrate that the alkyne [2 + 2 + 2] cycloaddition reaction catalyzed by dipimp (2-iminomethylpyridine ligand)/$CoCl_2$-$6H_2O$/Zn is applicable to polymerization, yielding linear polymers via a selective cross-cyclotrimerization reaction, which occurs in a chain-growth manner.

For controlled polymerizations by partially intramolecular cycloaddition that produce linear polymers via the reaction of AB-type monomers comprising monoalkyne and diyne moieties, directing alkyne reactivities towards selective cross-coupling over homo-cycloaddition is important. The selective cross-coupling between monoalkyne and diyne parts yields linear polymers. Alternatively, polymerization involving a self-coupling reaction forms linear and branched structures in a non-controlled manner.

We have succeeded in nearly complete control by substitutents of substrates for cross-cycloaddition, and applied it to design an AB-type monomer for the cycloaddition polymerization. The polymerization of such AB-type monomers catalyzed by the cobalt catalyst proceeded smoothly in a chain-growth fashion to provide linear polymers, achieving control over molecular weights and the polydispersity of the resultant polymers. The utilization of this method to the one-shot spontaneous block copolymerization of a mixture of two monomers has also been demonstrated. Currently, we propose a catalyst transfer mechanism for this polymerization, although the immortal polymerization mechanism cannot be ruled out. Further investigation on the reaction mechanism and application is underway.

Based on a high functional group compatibility with the catalysis, this method may be useful in preparing diverse functionalized polymers in a controlled manner.

Keywords: *Alkynes; Cycloaddition; Copolymerization; Homogeneous catalysis; Polymerization;*

P-0411

PREPARATION OF POLYCARBONATE WITH ANTHRACENE AND AZIDO PENDANT GROUPS AND ITS GRAFTING VIA CLICK CHEMISTRY

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This study deals with the synthesis of anthracene- and azide-functional cyclic carbonate monomers, anthracen-9-ylmethyl 5-methyl-2-oxo-1,3-dioxane-5-carboxylate and 2-azidoethyl 5-methyl-2-oxo-1,3-dioxane-5-carboxylate, by the reaction of anthracen-9-ylmethyl 3-hydroxy-2-(hydroxymethyl)-2-methylpropanoate and 2-azidoethyl 3-hydroxy-2--(hydroxymethyl)-2-methylpropanoate with ethyl chloroformate in tetrahydrofuran at room temperature, respectively [1]. The copolymerization of these anthracene- and azide-functional cyclic carbonate monomers was carried out successfully via ring-opening polymerization (ROP) using benzyl alcohol as initiator, 1,8-diazabicyclo[5.4.0]undec-7-ene and 1-(3,5-bis(trifluorometh1-(3,5-bis(trifluoromethyl))-3-cyclohexyl--2-thiourea, as catalyst system [2]. In addition, side chains were synthesized via atom transfer radical polymerization and ROP. The grafting reaction of these side chains with the anthracene- and azide- functional polycarbonate as a main chain was accomplished under facile conditions via click reactions (CuAAC and Diels-Alder).

The composition and molecular weight of the polycarbonates were characterized by ^{1}H NMR and GPC. Thermogravimetric analysis and differential scanning calorimetry measurements were used to investigate the thermal properties of the resulting polymers.

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Keywords: *Polymers; Polymerization;*

P-0412

ARYLSULFINATES AS REPLACEMENT OF ORGANOMETALLIC REAGENTS IN PALLADIUM-CATALYZED COUPLING REACTIONS

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Substituted biaryls are an important motif in a variety of pharmacophores, pesticides and chiral ligands. Palladium-catalyzed cross-coupling reactions employing stoichiometric amounts of organometallic reagents as nucleophiles are generally utilized for their synthesis. Therefore multi-step, expensive, moisture-sensitive and potentially toxic transformations are often needed to access these coupling partners. Decarboxylative cross-couplings have recently emerged as an alternative method to overcome these limitations. We successfully advanced this principle to the use of aromatic sulfinates salts as analogues of benzoic acids. Our efforts involving this desulfinylative coupling of substituted benzenesulfinates with aryl-bromides also led to the development of a catalytic homo-coupling of aryl-sulfinates under oxidative conditions. The scope of these reactions will be presented. Furthermore, their reactivity in aqueous media as a way to develop a more environmentally benign reaction will be highlighted.

Keywords: *Palladium; C-C coupling; Green chemistry; Sulfur;*

P-0413

SYNTHESIS AND INVESTIGATIONS OF MULTIPLE HYDROGEN BONDED SUPRAMOLECULAR HOST – GUEST COMPLEXES

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In supramolecular chemistry, molecular recognition via non-covalent binding sites such as hydrogen bonds is common. It is necessary to have complementary hydrogen bond acceptor (**A**) and hydrogen donor (**D**) patterns. A single hydrogen bond is relatively weak, but the combination of multiple hydrogen bonds can lead to stable host - guest complexes.[1]

Due to the existence of attractive and repulsive secondary hydrogen bonds, binding patterns with as many attractive secondary hydrogen bonds as possible are the target. An example with a DDDD-AAAA pattern shows an association constant of 10^5-$10^6 M^{-1}$.[2]

It is reasonable to synthesize molecules whose preferred conformation is the one which can form the highest number of hydrogen bonds. If an intramolecular bond has to be broken to get the needed binding pattern, a loss of energy at the expense of the complex stability would be the consequence.[3] Therefore, the aim should be to stabilize the preferred conformation by using, for example, intramolecular hydrogen bonds.[4]

Due to the orthogonality of the binding sites, highly specific dendrimeric systems could be generated.[5]

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Keywords: *Hydrogen bonds; Host-guest systems; Molecular recognition; Supramolecular chemistry;*

P-0414

IN SITU CLICK CHEMISTRY FOR HUMAN ACETYLCHOLINESTERASE INHIBITORS DISCOVERY

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In situ click chemistry is a new approach (K.B. sharpless *and coll. Angew. Chem. Int. Ed.* **2002**, *41*, 1053-1057) to lead discovery applied to target guided synthesis (TGS) that allows a biological target to assemble its own inhibitors. Indeed, in the presence of the targeted multisite enzyme and a series of building blocks bearing complementary reactive functions, ligands with the best affinities would react to form an irreversible bond. The enzyme serves as a template for the reaction.

Being implicated in the pathogenesis of the Alzheimer's disease, recombinant human (*rh*) strain of Acetylcholinesterase (AChE) is our enzyme of choice for the application of this concept. New Huprine (Hup) derivatives were found to be very potent AChE inhibitors, presenting IC_{50} values in the subnanomolar range (P.Y. Renard *and coll. ChemMedChem*, **2011**, *8*, 876-888). These acylation site inhibitors were tested for *in situ* click chemistry with known peripheral site ligands (tetrahydroisoquinoline, PIQ) in the presence of *rh* and mouse AChE. The *in situ* Huisgen reaction was successful, allowing the formation of two new potent heterodimeric inhibitors using for the first time human AChE. In addition, the click reaction occurred unprecedentedly in the gorge of the enzyme far from the acylation active site inducing different regioselectivities than those already described in the literature.

Furthermore, new click reactions are being explored such as the hetero Diels Alder reaction. Polysubstituted 3-hydroxypyridines scaffolds are obtained from the corresponding 5-alkoxyoxazoles and dienophiles. The reaction needs activation (thermal or catalytic) to form an irreversible bond, what makes it a very interesting target for *in situ* click chemistry since it should not proceed without the enzyme. Huprine derivatives bearing a terminal electron-poor olefin and PIQ derivatives a 5-alkoxyoxazole ring are being investigated for the *in situ* click chemistry approach with AChE as the target.

Keywords: *click chemistry; host-guest systems; inhibitors; enzymes; regioselectivity;*

P-0415

SYNTHESIS AND ABSORPTION CHARACTERIZATION OF NEW MIXED DERIVATIVES OF P-CHLORODIAZALINE CALIX[4]ARENES CONTAINING ACRYLOYL GROUPS

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Calixarene are macrocyclic molecules made up of *p*-substituted phenolic units linked by methylene bridges *ortho* to the OH functions.[1–3] They are known to provide useful building blocks for hollow molecular scaffolds with easily functionalizable hydrophilic and hydrophobic lower and upper rims, respectively.[4, 5] A series of acryloyl derivatives of calix[4]arene[6, 7] which is including the first examples of mixed *p*-chlorodiazaline esters. In the first step, *p*-tert-butylcalix[4]arene have been obtained by condenzation of *p*-tert-butylphenol and formaldehyde. In the second step calix[4]arene have been prepared by removing the *tert*-butyl group by the reaction of *p*-*tert*-butylcalix[4]arene with $AlCl_3$ according to reverse Friedel-Crafts reaction. The calix[4]arene compounds containing azo groups have been prepared by the reaction of diazotized *p*-chloroaniline with calix[4]arene in dry condition in order to 1:1, and 1:2 molar ratio. Acryloyl derivatives of azo calix[4]arene compounds have been synthesised by the reaction of azo calix[4]arene with metallic sodium and then acryloyl chloride in N_2 atmosphere in order to 1:1, 1:2, 1:3 and 1:4 molar ratio. The structures of these compounds have been characterized by elementel analysis, IR, UV-VIS, ^{1}H-NMR and ^{13}C-NMR.

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Keywords: *calix[4]arene; diazenyl; acryloyl chloride;*

P-0416

INVESTIGATION OF INOSITOL-PYROPHOSPHATE MEDIATED PROTEIN PYROPHOSPHORYLATION

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Inositol-pyrophosphates (PP_y-$InsP_x$) as secondary messenger are in sharp focus of biochemical research due to their importance in different cellular processes like apoptosis, telomere length regulation or cytoskeleton dynamics.[1] Furthermore, recent investigations showed nonenzymatic transfer of a phosphate moiety from a PP_y-$InsP_x$ on a phosphoserine residue generating a protein pyrophosphate.[2] The function of this post-translational modification is still unclear. One possibility to investigate this phenomenon would be the identification of a selective electrophilic trap for pyrophosphates. The design of probes for the tagging of sulfhydryl or thiophosphate groups with electrophilic traps has already contributed much to our understanding of cellular processes.[3] Based on this rationale, the development of strategies to tag pyro- or thiopyrophosphates will provide information about the targets and functions of this novel post-translational modification. We will present the synthesis of pyro- and thiopyrophosphorylated derivatives of e.g. serine and threonine. The reactivity of these compounds will be screened against different electrophiles to evaluate the specificity of the tagging in the presence of other nucleophiles. The knowledge obtained from these experiments will help us to develop selective tagging strategies for target proteins of PP_y-$InsP_x$ mediated phosphorylation in cellular extracts.

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Keywords: *Phosphorylation; Proteins; amino acids; Bioorganic chemistry;*

P-0417

SYNTHESIS OF 1H-PYRAZOLO[1,2-A][1,2,4]-TRIAZOL-8-IUM IONS FROM A ONE POT REACTION USING A DIPHOSPHORUS TRICATION SYNPHOS REAGENT

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Highly charged main group element centered cations can possess unusual reactivities.[1] We are especially interested in using cationic, highly-reactive P^{III} centered compounds (***S**yn**P**hos*) as reagents for unusual transformation reactions. The high oxophilicity of P^{III}-compounds allows deoxygenation and condensation reactions, which represents important transformations in organic synthesis. Recently, we developed the Janus-head type diphosphorus trication[2] $[pyr_3P_2]^{3+}$ (pyr = 1,3-dimethylpyrazole) and used it for the deoxygenation of phosphanoxides.[3] This reaction was accompanied with the transfer of a pyrazole moiety to yield novel pyrazolylphosphonium salts.[3] In this contribution, we present a novel access to 1*H*-pyrazolo[1,2-a][1,2,4]-triazol-8-ium ions using trication $[pyr_3P_2]^{3+}$ in condensation reactions of aldehydes and nitriles.

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Keywords: *Aldehydes; Phosphorus; Green chemistry; Synthesis design;*

P-0418

NOVEL BISPHOSPHINES FOR THE AMIDATION OF STERICALLY DEMANDING ARYL CHLORIDES

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The palladium-catalyzed amidation of sterically hindered, deactivated aryl chlorides with bulky aryl amides was achieved. This highly challenging transformation was accomplished using the novel [2.2]paracyclophane-derived unsymmetrical bisphosphine GemPhos in combination with a palladium(0) source.[1]

The catalyst system was exceptionally active for sterically demanding coupling partners. The ligand was further optimized featuring an electron rich and an electron deficient phosphino group. Those electronically reversed phosphine groups displayed synergistic behavior as evidenced from kinetic investigations. The transmetallation and the reductive elimination were identified as rate determining steps.[2]

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Keywords: *Phosphines; Amides; Cross-coupling; Palladium;*

P-0419

NOVEL REACTIVITY OF FRUSTRATED LEWIS PAIRS: LOW TEMPERATURE HYDROGEN ACTIVATION AND HYDROGENATION OF UNFUNCTIONALIZED DOUBLE BONDS

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The hydrogenation of unsaturated compounds is traditionally accomplished by transition metal catalysts. The activation of hydrogen by frustrated Lewis pairs (FLP) has emerged to a powerful tool as an transition metal-free alternative.[1] Despite the tremendous advances in this field, so that even for complex organic transformations[2] could be realized, the hydrogenation of unfunctionalized double bonds remained a challenge.

However, we succeeded in the low temperature hydrogen activation by electron deficient phosphines in combination with the Lewis acid tris(pentafluorophenyl)borane (**1**). The high reactivity of the frustrated Lewis pair was exploited in the hydrogenation of unfunctionalized double bonds even at room temperature.[3] Aliphatic as well as aromatic olefins and dienes were hydrogenated in excellent yields.

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Keywords: *Alkenes; Boranes; Hydrogenation; Phosphines;*

P-0420

FUNCTIONALIZATION OF BICYCLO[3.3.0]OCTANES AS KEY BUILDING BLOCKS IN NATURAL PRODUCTS AND SYNTHESIS OF NOVEL HYBRID MOLECULES

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Bicyclo[3.3.0]octane is a common building block in a variety of natural products and pharmaceuticals, for example in the macrolactams cylindramide[1] or geodin A.[2] Cylindramide has been isolated from the marine sponge Halichondria cylindrata. It is a macrocyclic lactam including an acyltetramic acid and a trisubstituted bicyclo[3.3.0]octene. This lactam shows significant cytotoxicity against B16 melanoma cells with an IC_{50} of 0.8 µg/mL. The total synthesis of cylindramide has been published by Cramer[1] in our research group in 2005. Geodin A is also a tetramic acid macrocycle isolated from the marine sponge *Geodia sp*. Unlike cylindramide it could only be isolated as geodin A Mg salt and it bears a methylene group instead of a methyl group.

Previous work on cylindramide A revealed that the bicyclo[3.3.0]octane unit as well as the tetramic acid macrocycle are essential for the biological activity of tetramic acid macrolactams.[3] Starting from readily available cyclooctadiene bicyclo[3.3.0]octane systems have been synthesised and further functionalized towards new hybrid molecules. Key step is a diastereoslective Shi-epoxidation followed by a selective epoxide opening. Biological essays will reveal if these compounds exhibit comparable or even increased biological activities.

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Keywords: *Natural Products; Asymmetric synthesis; Biological activity;*

P-0421

3-PYRANONE DIOXACORROLE - AN EXTRAORDINARY TRANSFORMATION OF 21,23-DIOXAPORPHYRIN

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A ubiquitous nature of furan places this heterocycle in a row of significant players involved in several widely explored aspects of current research in the organic chemistry, starting from the total synthesis of natural products ending on formation of extended π-systems responsible for an optoelectronic behaviour. Within these paths a reactivity of furan stays in the central point of investigation as that heterocycle takes a crucial role in the formation of other systems (oxidative reactions) but also a cycloaddition observed on a post-synthetic level and widely used in the total synthesis. Similarly, the reactivity observed with a support of Al_2O_3 is an example of derivatization on a surface of the solid used in the wide range of environment concerning reactions.

While comparing the modifiability of furan, a transformation of such heterocycle with subtly changed electronic structure i.e. as an integral part of oxaporphyrin(s) stays in opposite side of mentioned rules as this building block remains unreactive in such systems as the demands of macrocycle take control over the subunit independence. Nevertheless an application of alumina to dioxaporphyrin led to an extraordinary transformations observed for the first time in the porphyrin-like skeleton. Here we present an unprecedented example of the Achmatowicz reaction observed for 21,23-dioxaporphyrin giving a 3-pyranone dioxacorrole skeleton. The new macrocycle presents features characteristic for a non aromatic molecule, and formally is a product of addition of a water molecule followed by a sequence of transformation leading to formation of presented molecule. The coordination of palladium(II) forces the formation of an unstable tautomer obtained by a creation of a palladium(II)-carbon bond within the coordination cavity. Characteristic features observed for the macrocycle and its behaviour will be discussed based on the spectroscopic premises (NMR, UV-Vis) along with a single crystal analysis.

Keywords: *Macrocycles; Oxidation; Porphyrinoids;*

P-0422

FABRICATION AND CHARACTERIZATION OF LLDPE-MODIFIED NANOSILICA/LDPE/LLDPE FILM: MICROWAVABLE PACKAGING APPLICATION

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LDPE and LLDPE are popular applied in the flexible food packaging. Because there are strong, tough, clear, good moisture barrier and can be sealed with heat. However, they are poor gas barrier or moisture resistances are not enough to be able to preserve food. Therefore, the concept of this work was used the nanosilica applied in preparing LLDPE/nanosilica as a outer layer film for LLDPE reinforced nanosilica/LDPE/LLDPE multilayer film for microwavable packaging materials in future work. Therefore, the objective of this work was to study the optimal conditions for preparing linear low density polyethylene film reinforced with uncoated and coated nanosilica and LLDPE reinforced nanosilica/LDPE/LLDPE multilayer film on mechanical properties, Thermal properties, barrier properties and physical properties. The experiment of this work was divided into 4 main steps. First, coating nanosilica with vinyltriethoxysilane by internal mixer. Preparation of linear low density polyethylene film reinforced with uncoated and coated nanosilica which different silica quantities are 1, 3, and 5 phr by blown film extruder. Preparation of LLDPE/nanosilica as a outer layer film for LLDPE reinforced nanosilica/LDPE/LLDPE multilayer film And then the surface morphology of film was examined by SEM and contact angle of film was measure by optical contact angle measurement systems. The properties of the film were analyzed; oxygen permeability by OTR and water vapor permeability by WVTR. Tensile properties of film were examined by universal testing machine and thermal properties of film was characterized by TGA. Results indicated that addition at 1 phr of treated nanosilica into LLDPE matrix (LLDPE-nano-SiO_2 1 phr) presented the highest tensile strength, modulus and elongation of these films. LLDPE treated nano-SiO_2/LDPE/LLDPE multilayer film presented the lowest of water vapor permeability but presented the highest of oxygen permeability. However, LLDPE treated nano-SiO_2/LDPE/LLDPE multilayer film presented the highest of degradation temperature.

Keywords: *LLDPE film; Nanosilica; Vinyltriethoxysilane; Barrier properties; Mechanical properties;*

P-0423

GOLD AND SILVER CATALYSED REACTIONS OF PROPARGYLIC ALCOHOLS

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The 1,3-isomerisation of propargylic alcohols to enones is known as the Meyer-Schuster rearrangement. We have demonstrated efficient room temperature reaction conditions for the gold-catalysed Meyer-Schuster rearrangement (>30 examples) of a wide array of secondary and tertiary propargylic alcohols to the corresponding enones in generally excellent yields and with high *E*-selectivity.[2, 3] The methodology has also successfully been applied to the synthesis of two small natural products, Isoegomaketone (anti-inflammatory properties) and Daphenone (cytotoxicity against five human tumour cell lines).[3]

Primary propargylic alcohols rearrange to give highly reactive terminal enones, which can undergo conjugate addition reactions with nucleophiles to access β-substituted products through convenient one-pot procedures.[2, 3] The use of silver as a catalyst, instead of gold, promotes substitution of the electron-rich propargylic alcohol with various oxygen, carbon and nitrogen nucleophiles.[3] β-Hydroxyketones can be accessed *via* a gold-catalysed hydration, employing phenols as the reaction additive.[2, 4] This methodology has been developed for the synthesis of enantiomerically enriched β-hydroxyketones and the synthesis of a natural nonadecenetriol (antiprotozoal agent against Tyransome parasites).[4] The gold catalysed hydration offers an alternative to traditional aldol procedures with the benefit of tolerating the presence of other enolisable centres.

The full scope of the Meyer-Schuster rearrangement and the investigation into the role of protic additives in the gold and silver catalysed reactions of propargylic alcohols will be described in the presentation**.**

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Keywords: *Gold; Homogeneous cataylsis; Meyer-Schuster rearrangement; Propargylic alcohols; Silver;*

P-0424

SYNTHESIS OF FLUORINATED ANALOGUES OF 6-HETARYL-7-DEAZAPURINE NUCLEOSIDES

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Analogues of nucleosides are an important class of anti-tumor and anti-viral therapeutics. Recently, nanomolar cytostatic activity against a panel of cancer cell lines was shown in 6-hetaryl-7-deazapurine ribonucleosides.[1] The aims of this project were: **a**) further modification of the lead structure by replacement of the 2'-hydroxy group by isosteric fluorine; **b**) comparison of cytostatic activities of ribonucleosides and their fluorinated analogues. A synthetic route to 6-hetaryl-7--deazapurine 2'-fluoro-2'-deoxyribonucleosides was developed. A key intermediate 6-chloro-7-deazapurine 2'-fluoro-2'--deoxyribonucleoside **1** was synthesized starting from 6-chloro--7-deazapurine ribonucleoside **3** in 9 steps in 18 % overall yield. The synthesis started with silyl protection of 3'- and 5'-hydroxy group followed by oxidation of 2'-hydroxy group and stereoselective reduction to obtain silylated arabinonucleoside **2**.[2] Then, several protection and deprotection steps as well as fluorination of the 2'-hydroxy group with DAST were used to synthesize 2'-fluoro-2'-deoxyribonucleoside **3**. Fluoroderivative **3** was used as a starting material for Suzuki cross-coupling reactions with hetarylboronic acids under aqueous conditions. 6-Hetaryl-7-deazapurine 2'-fluoro-2'-deoxyribonucleosides were obtained in 37–88% yield. All 6 target compounds were tested for their cytostatic activity against cancer cell lines. None of the fluorinated analogues showed any cytostatic activity. The results lead to conclusion that 2'-hydroxy group is esential for cytostatic activity of 6-hetaryl-7-deazapurine ribonucleosides.

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Keywords: *nucleosides; fluorination;*

P-0425

COPPER-CATALYZED ENANTIOSELECTIVE CYCLOPROPANATIONS OF HETEROCYCLIC COMPOUNDS USING DIAZOACETATES

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A broad variety of biologically active natural products contain a cyclopropane moiety within their structure. It has been shown that this three-membered ring system can play a significant role for the activity of potential drugs. While the asymmetric cyclopropanation of simple olefins like styrene has been well developed, electron-rich heterocyclic substrates like N-protected pyrroles and furan derivatives proved to be a challenging task.[1, 2, 3] Herein we report highly enantioselective cyclopropanation reactions of aromatic, heterocyclic substrates using diazoacetates toward multiple functionalized bicyclic compounds, which proved to be versatile building blocks for natural product synthesis approaches,[4] as well as for the synthesis of β-aminocyclopropanecarboxylic acids (β-ACCs) toward foldamers.[5, 6] In order to gain mechanistic insight into this important type of reaction computational calculations with QM methods are under investigation at the moment.

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Keywords: *asymmetric cyclopropanation; diazoacetates; aza-bisoxazoline ligands; heterocycles;*

P-0426

CU(DAP)2CL AS EFFICIENT VISIBLE LIGHT MEDIATED PHOTOREDOX CATALYST

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Photochemistry has become an attractive field of research as well as an interesting tool in organic synthesis. As most of the recently reported reactions are employing photoredox catalysts which contain worthy transition metals such as ruthenium or iridium, more inexpensive alternatives are desirable.

Sauvage et. al. reported in 1987 the photodimerisation of para-nitrobenzylbromide using $Cu(dap)_2Cl$. Inspired by this work we further explored the catalytic scope of this catalyst. Upon irradiation with green light (LED 530 nm) the ATRA-reaction of various activated organobromides (tetrabromocarbon, diethylbromomalonate, α-bromoacetophenone) and organoiodines (perfluoro-iodo-alkanes) with olefins as well as the allylation of α-keto-bromides and –chlorides was successfully developed. The obtained halogenated photoadducts can be further converted to precursors that appear to be useful for cross coupling reactions such as Heck-coupling, Suzuki-coupling or Tsuji-Trost allylations.

Keywords: *Photochemistry; Copper; atom-transfer radical addition; allylation; redox chemistry;*

P-0427

TETRAHALOGENO-DIPHENYLGLYCOLURILS VERSUS N-HALOSUCCINIMIDES: METHYL-AROMATICS FREE RADICAL HALOGENATION BEHAVIOR.

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It is obvious that efforts to find efficient and selective methods to functionnalise organic compounds remain of high priority. In this sense, free radical reactions represent an important field of valuable methods. Nevertheless, in recent years we already observed a dramatic failure of bromination of some essential nitrogen heterocycles and bis-heterocycles building blocks often involved in the synthesis of metallo-supramolecular structures. In this sense, *1,3,4,6*-tetrachloro and *1,3,4,6*-tetrabromo-*3*α*,6*α-diphenylglycolurils smooth halogen-oxidizers have been exploited in a new direction as reagents for free radical substitution towards some *N*-halosuccinimides non-reactive *bis*-heterocycles. An unexpected selectivity and reactivity were observed with methyl-benzenes, methyl-heterocycles and methyl-*bis*-heterocycles of interest. Crystal structure of *1,3,4,6*-tetrachloro-*3α,6*α-diphenylglycoluril was accurately determined from high resolution X-ray diffraction data at 100 K. Ab initio calculations were also performed in order to reveal the halogen···halogen interaction properties in this last compound. Electron and electrostatic features were carefully analyzed.

Keywords: *halogenation; heterocycles; Density functional calculations; radical reactions; charge transfer;*

P-0428

SHORT SYNTHESIS OF DILACTAMS-LINKED SUCROSE MACROCYCLES

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Sucrose, an inexpensive natural optically pure compound, is a promising building block for the preparation of chiral macrocyclic receptors.[1, 2] In the present communication the synthesis of optically pure macrocyclic derivatives with sucrose scaffold is presented.

The synthesis was initiated from 1',2,3,3',4,4'-hexa-O-methylsucrose (readily obtained from free sucrose by sililation-methylation-desililation) in which the secondary and 1'-OH hydroxyl groups were protected as methyl ethers. 1',2,3,3',4,4'-Hexa-O-methylsucrose was converted into 1',2,3,3',4,4'-hexa-O-methyl-6,6'-di-O-(methylsulfonyl)sucrose. Its condensation with 2 equiv. of the proper nitro- or cyanophenoles (o-, m-, p- respectively) provided the expected 6,6'-di-O-nitrophenyl-1',2,3,3',4,4'-hexa-O-methylsucroses and 6,6'-di-O-cyanophenyl-1',2,3,3',4,4'-hexa-O-methylsucroses, reduction of which afforded the corresponding di-amines. Condensation of these compounds with isophthaloyl or 2,6-pyridinedicarbonyl dichloride furnished the desiredmacrocyclic bis-lactams.

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Keywords: *sucrose; macrocycle; dilactams; isophthaloyl dichloride;*

P-0429

MICROWAVE-ASSISTED SELECTIVE OXIDATION OF DEOXYCHOLIC ACID

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Promotive action of bile acids on the transport of some drugs through the cell membrane attracted huge attention in pharmaceutical sciences. Such promotive action of bile acids was further increased by replacing hydroxyl groups with oxo groups yielding derivatives with lower hydrophobicity[1].

Synthesis of such bile acid derivatives with conventional experiments is generally time consuming giving low or moderate yield[2]. The aim of this work is in applying microwave technology in some reactions for selective oxidation of deoxycholic acid. Reactions have been performed in Discover Bench Mate microwave reactor (CEM, maximum output power 300 W, Synergy software) in closed-vessel system. Microwave process vials, with operating filling volume from 2-5 mL, have been used as reaction vessel.

Pure product of 3α,12α-diformyloxy-5β-cholanoic acid was obtained in quantitative yield from 3α,12α-dihydroxy-5β--cholanoic acid (deoxycholic acid) by dissolving it in methanoic acid and heating at 55ºC in microwave reactor for 30 minutes. Compared to the conventional heating experiments the presence of an acidic catalyst, like perchloric acid, was unnecessary. In the next phase, a partial deformylation of 3α,12α-diformyloxy-5β--cholanoic acid with sodium-hydroxide in acetone was achieved at 60 ºC during 5 minutes. Microwave-assisted selective oxidation with N-bromosuccinimide in *terc*-butanol and further deformylation gave 12α-hydroxy-3-oxo-5β-cholanoic acid in high yield and purity. Compared to the conventional protocol a remarkable reduction in overall processing time from hours to a few minutes was achieved. Structures of synthesized bile acids have been confirmed by ^{1}H- and ^{13}C- NMR spectroscopic data.

Acknowledgments: *This work was supported by a research grant from the Ministry of Education and Science of the Republic of Serbia (Grant No. 172021).*

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Keywords: *Oxidation; steroids;*

P-0430

SYNTHESIS OF 15-SUBSTITUTED ESTRONE DERIVATIVES

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Study of the estrogen receptors ERα and ERβ has been recently of considerable interest, because both receptors play a crucial role in female and male reproductive systems, regulate some key processes during development, and are important factors in certain types of cancer. ERα mediates the action of estrogens in classical tissues like uterus and mammary gland and it is also a traditional target for therapy of breast cancer as it promotes proliferation of certain healthy and cancerous tissues. On the contrary, ERβ is found in the ovary, brain, cardiovascular system, prostate and blood cells. In this respect, development of new ligands capable of selective binding to these receptors is of general interest. The preferential attention has been devoted to 17-substituted estradiol derivatives.[1, 2] In this respect 15-substituted estradiols or estrones constitute an interesting but hitherto mostly unexplored[3] class of compounds that might serve as potential ligands for the estrogenic receptors.

Our approach to the 15-substituted estrone derivatives started with the synthesis of 15β-vinylestrone that was greatly improved in comparison with the original procedure. The presence of the terminal double bond makes this compound an ideal substrate for cross-metathesis reaction with other terminal olefins as means for the attachment of variously substituted side-chains. As olefins were used alkenes or fluorinated alkenes, styrenes and their substituted congeners. In this manner we were capable generating a series of variously substituted 15β-estrone derivatives in good yields. Some of the prepared compounds were subjected for binding testing to ERα, ERβ, and other steroidal receptors.

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Keywords: *metathesis; steroids;*

P-0431

ANTIOXIDATIVE ACTIVITY OF SUBSTITUTED 5-AMINOPYRIMIDINES AND THEIR OXIDATIVE SELF-CONDENSATION IN DIMETHYL SULFOXIDE

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Pyrimidine heterocyclic nucleobases are the basic building blocks of nucleic acids, but they also work as coenzymes or high-energy molecules. Modified pyrimidines display a wide range of biological properties such as antiviral, cytostatic or antimicrobial activities. In this work we have observed the antioxidative effects of a series of substituted 5-aminopyrimidines using *in vitro* (TEAC, LPO) and cell-based assays. 2,4,6-trisubstituted 5-aminopyrimidines have been discovered as the most active in the TEAC (direct scavenging of long-lived radical) and LPO (compounds ability to protect rat liver microsomes against the Fe^{2+}/O_2-induced lipid peroxidation) assays but not in cell-based assay probably because of lower cell membrane permeability. Hence, the compounds which contained “protected” 5-aminogroup by a lipophilic substituent actually acted like a potential prodrugs, and the oxidative stress of Hep G2 cells was decreased. On the other hand, in cell-free assays the antioxidative activity of potential prodrugs was not found which is in agreement with the fact that the presence of “free” aminogroup in position 5 on pyrimidine skeleton is necessary for the antioxidative ability of the studied compound. Surprisingly, the active compounds were decomposed in dimethyl sulfoxide (DMSO) to deeply coloured and highly insoluble products. DMSO can act as an oxidation agent, but the ability of DMSO to oxidize 5-aminopyrimidines has not been described till now. We determined the structures of the products obtained by the DMSO oxidation of 5-aminopyrimidines. The 5-aminogroup can be oxidized to a keto group and a subsequent condensation with another molecule of an aminopyrimidine leads to tricyclic pyrimidinopteridines condensation products. The reaction rate of the oxidation-condensation reaction correlates well with the antioxidant activities of the 5-aminopyrimidines.

Keywords: *5-aminopyrimidines; antioxidants; lipid peroxidation; DMSO oxidation; pyrimidopteridines;*

P-0432

A REINVESTIGATION OF THE REGIOSELECTIVE SYNTHESIS OF TRIMETHOXYISLANDICIN

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The mould metabolite islandicin[1] represents a key substructure of anthracycline tumour antibiotics. Thus it is not surprising that the total synthesis of this compound has been extensively investigated, resulting in several described synthetic methods for unsymmetrical anthraquinones. Nevertheless, there is still a controversy[2] about reaction regiospecificity, which is required to obtain unambiguous relative positions of the methoxy group on the one side of the ring system and the methyl group on the other. Our interest in an efficient industrial synthesis of anthracyclines prompted us to reinvestigate the synthesis of trimethoxyislandicin.

Our synthetic sequence started with 2,3-dimethylanisole, which prove to be a superior source for 3-methoxyphthalic anhydride. The key step of the reaction was a Friedel-Crafts acylation of the anhydride with 2,5-dimethoxytoluene. This reaction was studied carefully both with respect to overall regioselectivity and yield of the desired regioisomer. A modification of the anthraquinone ring closure was worked out, which allowed carrying out the ring closure reaction and the preceding reduction in one pot, followed by oxidation to yield the title product.

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Keywords: *Regioselectivity;*

P-0433

SYNTHESIS OF OLIGOPHENYLENEETHYNYLENES WITH TERMINAL THIOESTER GROUPS FOR SINGLE MOLECULE SPECTROSCOPY

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The variation of the length of oligomers with phenyleneethynylene units (OPEs) presents an excellent possibility to analyze the changes of the physical properties as a function of molecule length. Using single molecule spectroscopy, we want to study the charge transport properties of OPEs connected to two gold electrodes using a mechanically controlled break junction method.[1] For the synthesis of such defined oligomers, a stepwise building is necessary. That includes Pd-catalyzed coupling reactions and acetylene deprotecting reactions.

To analyze the OPEs using single molecule spectroscopy we designed OPEs with terminal thioester groups able to bind to gold surfaces. The purification of these OPEs is of highest importance, and best performed by recycling gel permeation chromatography (rec. GPC).

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Keywords: *Single-molecule studies; Conducting materials; electron transport; Alkynes;*

P-0434

AXIAL-CHIRAL CONCAVE 1,10-PHENANTHROLINES

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The three-dimensional concave environment of the active centre of enzymes is to a large extent responsible for their high selectivity. That is why this concept was imitated for the design of concave reagents.[1] These concave macrocyclic, mostly bimacrocyclic, compounds can be compared to a “lamp” with the concave environment as the “lampshade” and the active centre as the “light bulb”. Structurally, these concave reagents are much less demanding than enzymes, but they are also much more stable concerning different influences like pH or temperature.

Concave 1,10-phenanthrolines are one group of concave reagents. Their concave shape is realized by phenyl bridgeheads in the 2- and 9-position of the 1,10-phenanthroline which are connected by ethylene glycol or methylene chains.

Achiral variants of concave 1,10-phenanthrolines were successfully used as ligands for diastereoselective metal catalysis.[2, 3]

It is our new aim to enable enantioselective catalysis. Therefore, it is necessary to build an axial-chiral cavity, which can be realized by the introduction of one naphthyl bridgehead.

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Keywords: *Supramolecular chemistry; Macrocycles; Enantioselectivity;*

P-0435

NOVEL ARTESUNIC ACID HOMODIMERS AS POTENT ANTI-LEUKEMIA AGENTS

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Cancer claims the lives of many people every year, hence great effort is put into the development of effective drugs against these diseases and therefore new lead structures of active compounds are of significant value. Representatives of the 1,2,4-trioxane family, like artemisinin and its semi-synthetic analogue artesunic acid (or artesunate), are impressive examples for compounds known to be highly active against cancer. The innovative concept of hybridization, meaning the connection of bioactive natural products (fragments) by at least one carbon-carbon bond, can be applied to artesunic acid. It has been shown by the Tsogoeva group in 2010, that dimers of artesunic acid are more effective against leukemia cells than artesunic acid itself and that they evade the problem of multidrug resistance of leukemia cells in contrast to some known anti-cancer agents. As a follow-up, we decided to synthesize three new homodimers of artesunic acid, connected by three different linkers (aliphatic, aromatic and alcoholic),to gain knowledge about the linker's contribution to the anti-cancer activity.

To obtain these molecules, artesunic acid was coupled with the corresponding diamine linkers, applying amide-bond-coupling conditions, and the three desired homodimers could be obtained in good yields (83 – 88%). After biological activity tests against thehuman leukemia cells CCRF-CEM and the multidrug resistant one CEM/ADR5000, we realized, that the shorter the linker, the more active the homodimer is against the two cell types. This insight and the successful application of the hybridization concept on artesunic acid takes us a significant step forward in the design of aforementioned new lead structures against cancer.

Keywords: *Artesunic acid; homodimers; anti-cancer agents;*

P-0436

SYNTHESIS OF CHIRAL TH-SYMMETRICAL HEXAKIS ADDUCTS OF C_{60}

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Hexakis adducts of C_{60} with an octahedral addition pattern, a motif which is unique in organic chemistry, represent attractive 3D building blocks for the construction of Covalent Organic Frameworks (COFs).[1] The combination of these highly symmetrical hexakis adducts with a rigid linear spacer can lead to the formation of extended organic frameworks with a cubic topology while the formation of other possible structures will be suppressed. Furthermore, if the addends of the building blocks bear stereogenic centers and are optically pure then the corresponding COF will be equipped with this element of chirality.

Our target is the synthesis of hexakis adducts of C_{60} bearing functional groups with well-defined geometry. For this purpose, we designed three novel optically pure cyclo-[1]-malonate esters bearing C8, C12 and C14 spacers. The malonate esters were synthesized *via* the condensation reaction of malonyl chloride with the appropriate optically pure diols.[2]

Subsequently, a six-fold Bingel reaction with C_{60} was performed, leading to the corresponding T_h-symmetrical hexakis adducts. Their acetal deprotection under acidic conditions will lead to the fully deprotected fullerene adducts, where the 1,2-diol moieties will be arranged in an octahedral well defined geometry.

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Keywords: *[60]fullerene; Hexakis-adduct; Chiral; COF;*

P-0437

SYNTHESIS OF BIPHENOLS THROUGH SUZUKI-MIYAURA-REACTIONUSING PD/C IN WATER

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Biphenols and their derivativesare lead structures in many natural products, drugs (e.g. vancomycin) andprecursor of many ligands.[1]

A good method to synthesise biarylsis the Pd-mediated Suzuki-Miyaura-reaction.It has been shown that electron-rich arylhalides are less reactive, especiallyphenolates under the basic conditions of the Suzuki-Miyaura-reaction.In the majority of reactions the phenolic hydrogen was masked by a protecting-group,followed by the aryl-aryl-coupling and the deprotection of the phenol (3steps). In the case of biphenols actually only a few examples of a direct onestep coupling are known, avoiding the protection/deprotection-steps.[2]

We report an efficient methodfor the synthesis of biphenols in one step and in good to excellent yields,inspired by the green protocol of Hirao,a ligandless Suzuki-Miyaura-reactionusing simple Pd on charcoal (heterogenous, easy to remove) in water.[3]Thereby the basic conditions (K_2CO_3) enhance the solubilityof the phenolic substrates.

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Keywords: *Palladium; Borates; Water chemistry; Heterogeneous catalysis; Biaryls;*

P-0438

EVALUATION AND OPTIMIZATION OF VARIOUS APPLICABLE CROSSLINKERS ON GELATION TIME OF POLYACRYLAMIDE GEL

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In this work, various polymer gels were prepared by crosslinking of aqueous solutions of polymer and crosslinker for the purpose of water shut off treatment in oil fields. A co-polymer of 2-acrylamido-2methyl-propanesulfonic-acid sodium salt (AMPS) and acrylamide (PAMPS) was used as polymer and chromium triacetate, polyethyleneimine (PEI) and hexamethylenetetramine (HMTA) were used as a metallic crosslinker and organic crosslinkers, respectively. In order to predict the gelation time of these three polymer gels, central composite design (CCD), the most popular form of Response Surface Methodology (RSM), was applied for the experimental plan. Three quadratic models were presented for the three polymer gels which was highly significant. Therefore, the main effects and the interactions between the factors were also identified. The results showed that the polymer concentration was the main effect in all polymer gels. The interaction between the two factors (polymer concentration and crosslinker/polymer ratio) had the most effect on the gelation time of chromium triacetate polymer gel, while it had less effect on the gelation time of PEI polymer gel and negligible effect on the gelation time of HMTA polymer gel. It was also found that increase of polymer concentration and crosslinker/polymer ratio caused a decrease in the gelation time of HMTA polymer gel. However, selecting a suitable ratio for the factors of PEI and chromium triacetate polymer gels was essential for obtaining the optimum gelation time with a purpose of maximizing it. According to the optimization of polymer gels separately, the 13172 ppm concentration of polymer and 0.44 ratio of chromium triacetate/polymer resulted to the gelation time of 34 hr. Moreover, the 13208 ppm concentration of polymer and 0.16 ratio of PEI/polymer and the 13190 ppm concentration of polymer and 0.17 ratio of HMTA/polymer resulted to the gelation time of 8.3 hr and 25 hr, respectively.

Keywords: *Polymer Gel; Gelation Time; Chromium Triacetate; Polyethyleneimine; Hexamethylenetetramine;*

P-0439

SELF-ASSEMBLY OF A SUPRAMOLECULAR HEXAMERIC ENTITY: FORMATION, STRUCTURE AND PROPERTIES

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Molecular self-assembly is a powerful tool to generate order by using various types of interactions, such as hydrogen bonds, donor-acceptor or coordination interactions. It is a multistep process that is driven by the formation of selective, spontaneous and reversible association between the individual molecular components.[1]

We have discovered a case whereby a multisite hydrogen bonding molecular component **L** forms a well-defined hexameric species $\mathbf{L_6}$ in a strongly selective process. We describe here the assembly, the structure and the features of this entity, self-assembled from two variants $^{3}\mathbf{L}$ and $^{9}\mathbf{L}$ differing only by the length of the four hydrocarbon chains attached to the core, propyl and nonyl respectively.

The compounds $^{3}\mathbf{L}$ and $^{9}\mathbf{L}$ have been described earlier and are known to form supramolecular polymers in solution[2] or on surfaces[3] when combined with an equimolar amount of a ditopic monomer capable of establishing six hydrogen bonds with one of their terminal subunits. The two molecules have been fully characterised in polar solvents as well as in the solid state after crystallisation from such solvents. Nevertheless, their full potential is yet to be realised, as indicated by their ability to self-assemble into a well-defined hexameric species $^{3}\mathbf{L_6}$ and $^{9}\mathbf{L_6}$ under other conditions.

In the work presented here, we discuss the nature of this new and complex hexameric assembly, paying particular attention to its stability as a function of temperature and other chemical stimuli.

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Keywords: *Supramolecular chemistry; Self-assembly;*

P-0440

MULTIPLY TWISTED (LK > 1) MÖBIUS MOLECULES

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The credit of introducing the Möbius topology to chemistry goes to Heilbronner. As a consequence of his theoretical predictions,[1] the original Hückel rule is reversed for Möbius annulenes. Or more precisely, cyclic conjugated systems with $Lk = \text{odd}$ are aromatic with $4n$ and antiaromatic with $4n+2$ π-electrons. A number of theoretical articles followed, but not before 2003 a synthesis of the first aromatic Möbius molecule ($Lk = 1$) could be accomplished.[2] Initiated by this breakthrough the concept of Möbius topology has gained further attention. Recently, a number of Möbius porphyrins were published by Latos-Grazynski[3] and Osuka[4]. However, multiply twisted ($Lk > 1$) Möbius molecules are still elusive, and therefore they are challenging synthetically targets. Starting from the topology of the "Boy surface" we developed an instruction guide to assemble a triply twisted ($Lk = 3$) Möbius molecule.

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Keywords: *Macrocycles;*

P-0441

A POTENTIAL MECHANISM FOR 5-METHYLCYTIDINE DEMETHYLATION IN DNA

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C5-Methylation of 2'-deoxycytidine (dC) in DNA to form methyl-2'-deoxycytidine (mC) is a well-known process, which is involved in gene expression and genomic imprinting.[1] By way of contrast the active removal of this methyl group to erase epigenetic marks is barely understood. One possible mechanism involves base excision repair, which could cut out mC and replace it by dC. However, this includes generation of strand breaks and therefore could lead to genomic instability. One also more atom-economic pathway would be the conversion of the methyl-residue into a good leaving group. Consequently the elimination of non-toxic CO_2 was put into focus after the discovery that TET-enzymes oxidize mC to 2'-deoxycarboxycytidine (caC) via the hydroxymethyl- and formyl derivatives.[2, 3, 4]

To prove the existence of such a decarboxylation pathway in biological systems a [$^{15}N_2$]-labeled caC phosphoramidite was synthesized in 14 steps and incorporated into oligonucleotides. These strands were incubated with mouse embryonic stem cell (mESC) extract (or non-mESC extract as control), re-isolated via a clicked biotin-label and digested. The resulting nucleoside mixture was analyzed by a HR-HPLC-MS based isotope tracing method. Whereas in the negative control no ^{15}N-labeled dC was detectable, incubation with mESC extract resulted in [$^{15}N_2$]-dC which can only be formed by decarboxylation of [$^{15}N_2$]-caC. To gain deeper insight into a potential reaction mechanism, chemical studies with a caC nucleoside and DNA were performed. Without saturation of the C5-C6 double bond of caC no decarboxylation could be observed in these experiments. The saturation can be obtained transiently by C6 addition of a thiol (for example cysteine), which re-eliminates after decarboxylation. Furthermore the presence of imidazole (as in histidine) or an amine (as in lysine) is essential, which suggests a proton catalyzed mechanism.[5] Consequently the active center of the postulated decarboxylase should contain a nucleophilic center and residues capable of proton catalysis.

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Keywords: *DNA methylation; Bioorganic chemistry; Imprinting; isotopic labeling; mass spectrometry;*

P-0442

CARBOXYLATE-ASSISTED RUTHENIUM-CATALYZED HYDROARYLATION OF UNACTIVATED ALKENES BY C-H BOND FUNCTIONALIZATION

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Chelation-assisted catalytic C-H bond functionalizations have emerged as a powerful tool for direct arene derivatization.[1] Whereas direct C-H bond alkylations [2] has been developed as a sustainable alternative to traditional transition-metal-catalyzed cross-coupling reactions between organometallic reagents and alkyl halides, C-H bond additions to multiple C-C bonds by hydroarylations represents one of the most atom-economical approaches to alkylated arenes.[1]

Since the seminal work on ruthenium-catalyzed hydroarylations by Lewis and Murai[3] various catalytic systems have been devised for this challenging transferreaction[4]. Despite this progress the hydroarylation of unactivated alkenes continues to require harsh reaction conditions, while electronically activated alkenes have successfully been utilized under milder reaction conditions.

Herein we present a ruthenium catalyst for the hydroarylation of unactivated alkenes, which operates under mild reaction conditions and displays a broad functional group tolerance. Thus, several electron-rich and electron-deficient arenes were alkylated in a highly chemo-selective fashion. Furthermore, valuable functional groups, such as ethers, ketones, esters and halides now were tolerated.

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Keywords: *C-H activation; Ruthenium; Homogeneous catalysis; Sustainable Chemistry; Alkenes;*

P-0443

CHROMATOGRAPHIC INVESTIGATIONS ON THE PHOTODEGRADATION BEHAVIOR OF IRIDIUM BASED TRIPLET EMITTERS

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In the last few years, the choice of products using OLED-technology increased rapidly: from mobile phones, TVs and digital cameras to lighting devices and diverse car equipment. But to become a competitive technology on the world market, it is an imperative to overcome the still remaining problems concerning the operational lifetimes of OLEDs. Many attempts have been made so far, to shed light on the degradation mechanisms, studying the physical and chemical changes in the device.

Regarding emitter degradation, two different mechanisms attracted attention: the degradation via the excited state and the chemical degradation caused by highly reactive species like in situ formed radicals or singlet oxygen. To gain some insight into the correlations between the degradation types and the compound structures, we established a chromatography based screening setup to analyze the degradation behavior of emitter complexes under different conditions. We used well known iridium complexes of different emission energies for the screening in a variety of solvents under inert as well as ambient conditions. After irradiation, the dissolved samples were subjected to our screening setup where the complexes were chromatographically separated from degradation products (HPLC). Analysis of the degradation rate and products were performed via DAD detection and Q-TOF mass spectrometry. The obtained data enables us to draw conclusions regarding the mechanisms and processes responsible for the emitter degradation and may help in future to predict emitter stabilities in a reliable way.

Keywords: *iridium; analytical method; mass spectrometry;*

P-0444

SYNTHESIS AND PROPERTIES OF BICHROMOPHORIC MACROCYCLES

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Conjugated polymers have attracted increased attention in the last decades due to interesting optical and electronic properties. Although these compounds are applied in OLEDs and photovoltaics nowadays, some of the fundamental physics like the interchain interaction in highly-concentrated solutions or in films still remains controversial.[1]

We have synthesized and investigated model dimers of conjugated oligomers, linked in a macrocyclic scaffold. Two monodisperse conjugated oligomers, based on phenylene-ethynylene-butadiynylene entities are intramolecularly fixed by rigid clamp units, providing a defined distance. The size and distance of the chromophores can be defined synthetically.[2]

The final ring closure towards the target structures is achieved by an intramolecular oxidative coupling of rigid bisacetylenes in a Pd-mediated coupling reaction. The bichromophoric systems and linear model compounds are purified by recycling GPC and fully characterized and visualized by means of NMR, MALDI-TOF-MS, GPC and STM.

All bichromophoric systems and linear model compounds are investigated by optical spectroscopy in detail, using both time resolved and single molecule luminescence techniques. The most closely spaced chromophores show a slight red shift and a slowing of fluorescence lifetime, indicating the formation of a weak intramolecular excimer or H-aggregate. Intramolecular energy transfer is monitored for the acyclic bichromophoric system by a rapid fluorescence depolarization. Energy transfer is also detected for the cyclic bichromophores by low temperature single molecule fluorescence spectroscopy.[3]

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Keywords: *macrocycle; conjugated oligomers; Pd catalyzed reaction; optical spectroscopy;*

P-0445

NITROALDOL REACTION AS A KEY STEP IN THE SYNTHESIS OF RARE DIAMINO SUGARS

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Host-pathogen interactions are mediated by biopolymers attached to the cell membrane of bacteria. These complex molecules consist of different carbohydrates and fatty acids with a variety of linkage types.[1] Among the involved carbohydrates polydeoxy-polyamino sugars play an important role. Since their isolation from natural sources is usually demanding and purification of these rare molecules often fails due to non-separable impurities, chemical synthesis has to supply appropriate glycopolymers.[2] The synthesis of these targets is still a challenge for synthetic chemists. Herein we present a straightforward route towards diamino trideoxy sugars using a nitro aldol reaction. We synthesized the L-threonine derived aldehyde by applying the Garner protocol[3] which was further converted into the target molecule using 2-nitroacetaldehyde diethylacetal under basic conditions to establish the carbon backbone. The reduction of the nitro group with Raney-nickel and subsequent peracetylation led to a fully protected derivative of 2,4-diamino-2,4,6-trideoxy-D-galactose. The D-*galacto* configuration was assigned by NMR-spectroscopy. After a deprotection step the free di-*N*-acetylated carbohydrate as well as the corresponding ethylglycosides were isolated, depending on the reaction conditions applied.

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Keywords: *Carbohydrates; Amino acids; Aldol reaction;*

P-0446

PHOTOCATALYTIC ARYLATION OF ALKENES, ALKYNES AND ENONES WITH DIAZONIUM SALTS

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An efficient visible-light-mediated radical arylation of unsaturated compounds in presence of aryl diazonium salts and $[Ru(bpy)_3]^{2+}$ (“bpy” is 2,2'-bipyridine) or eosin Y as photocatalysts under irradiation with blue or green light is reported. An aryl diazonium salt is reduced by the photoexcited state of the photocatalyst giving an aryl radical which can subsequently add to olefins, acetylenes and enones. Reoxidation of the intermediary formed radical by the catalyst followed by deprotonation of the carbenium ion gives the arylated product. Alkenes and enones undergo sp^2-sp^2, alkynes undergo sp^2-sp cross-coupling. The reaction of phenyldiazonium salt with styrene gives stilbene, for example. The coupling of unsaturated compounds and aryl diazonium salts is an experimentally simple procedure which is characterized by high yields, low catalyst loadings and mild conditions using visible light and ambient temperature. The one-electron oxidation and reduction photoredox process improves a classic Meerwein arylation protocol significantly.

Keywords: *photocatalysis; arylation; diazonium salts; radicals; visible light;*

P-0447

IN SITU GENERATED DIOXIRANE ORGANOCATALYSTS IN ENANTIOSELECTIVEEPOXIDATION REACTIONS

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Organocatalysis has become a viable strategy for the preparation of epoxides.[1] Using carbonyl groups and Oxone generating the corresponding dioxiranes *in situ* provides an effective organocatalytic access.[2] We could identify a new catalytic moiety (4-(trifluoroacetyl)benzoic acid) based on this concept. In our efforts to develop multicatalysis approaches,[1c,3] a peptide-like catalyst was synthesized to optimize the reaction conditions for the epoxidation of 1-phenyl-1-cyclohexene (20 mol% catalyst, 20 mol% TBABr, Oxone (3 equiv), $NaHCO_3$ (4.6 equiv.), DCM/H_2O (1:1), 5 h, r.t., 95% conversion). In an attempt to improve enantioselectivity, both functionalized peptide catalysts containing a non-natural adamantane amino acid and C_2-symmetric difunctionalized diamine catalysts have been synthesized.

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Keywords: *Epoxidation; Organocatalysis; Peptides; Enantioselectivity;*

P-0448

SYNTHESIS OF INTERLOCKED MOLECULES CONTAINING SHAPE-PERSISTENT MACROCYCLES: A COVALENT TEMPLATE APPROACH TOWARDS ROTAXANES

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Interlocked molecules like rotaxanes or catenanes have been attracting chemists' interests since their discovery due to their extraordinary shape, the synthetical challenge, and promising chemical-physical properties, particularly in the context of artificial devices like molecular machines. A lot of template directed syntheses using weak interactions e.g. metal coordination or hydrogen bonding, were established, whereas routes using covalently bonded templates were mostly rejected. Recently, a renaissance of this pioneer approach arose and the capability of this method was confirmed by several published applications.

Our group employed covalently bonded templates successfully for various purposes, particularly in syntheses towards shape-persistent macrocycles or macrocycle encapsuled polymers.[1] Based on this earlier work, now we used covalently bonded templates in the synthesis of a novel [2]rotaxane containing rigid macrocycles. A centered phenylene–ethynylene macrocycle is threaded onto a phenylene-ethynylene rod axis and macrocyclic stopper units prevent a slippage effectively. The synthetic approach relies on the centered macrocycle being connected *via* phenolic ester bonds to the axis and subsequently a selective bond cleavage by nucleophilic substitution at the carbonyl group leads from the prerotaxane to the rotaxane.

The formation of the rotaxane was confirmed by MALDI-TOF-MS, ^1H NMR and GPC. Additionally, we visualized the [2]rotaxane by scanning tunneling microscopy at the solid/liquid interface of 1,2,4-trichlorobenzene and highly oriented pyrolytic graphite.

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Keywords: *Rotaxanes; Macrocycles; Template synthesis; Conjugation;*

P-0449

SYNTHESIS OF NEW FLUORESCENT BUILDING BLOCK BASED ON CHOLESTEROL, PHENYLALANINE AND COUMARINE

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Cholesterol as a fundamental steroidal unit remains in interest of both organic chemists and biochemists. It is known, that cholesterol derivatives represent model and emerging class of chiral liquid crystals. Moreover, this highly lipophilic compound may serve as molecule which helps to deliver certain pharmacophore to targeting tissue. In this labor as a central linker 4-azido or 4-iodo L-phenylalanine were used. The α-amino group of L-Ala was derived in both cases by fluorescent coumarine marker, aromatic azide was introduced into Huisgen 1,3-dipolar cycloaddition and iodo derivative into Sonogashira cross-coupling reaction with propargylated cholesterol. These compounds themselves may well be interesting from both, the supramolecular point of view, as well as, subsequent derivatization which is enabled due to the carboxylic acid functionality remains the only non-derived unit in the molecule.

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Keywords: *cholesterol; fluoprescence; click chemistry; cross coupling;*

P-0450

EFFICIENT SYNTHESIS OF NEW POLYHYDROXYLATED FLAVON-3-OLS

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The flavonoids are prominent components of citrus fruits, seeds, olive oil, tea, red wine and other food sources. They are part of the human diet and can show important beneficial effects on human health[1]. The flavonols are a subclass of this family of low molecular weight compounds, which have a 3-hydroxyflavone backbone. These oxygen heterocyclic compounds have been identified as fulfilling most of the necessary criteria to present a strong antioxidant activity, because they present a C2=C3 double bond conjugated with the 4-keto group, an *ortho*-dihydroxy-substitution on ring B and free OH groups at the C-3 and C-5 positions[2]. Examples of some well-known naturally occurring flavonols are quercetin, kaempferol, myricetin, among others.

In the present work, 3-hydroxyflavones were prepared through a two-step synthetic route, namely an aldol condensation of appropriate 2'-hydroxyacetophenones and benzaldehydes[3] and an Algar-Flynn-Oyamada reaction[4], ending with the cleavage of the protecting groups. The experimental procedures and results of this study as well as the structural characterization of the new compounds will be presented and discussed in this communication.

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Keywords: *Antioxidants; Cyclization; NMR spectroscopy; Oxygen heterocycles; Protecting groups;*

P-0451

PHOTOCATALYSIS WITH FLAVINS: HIGH-POWER-REDUCTIONS

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One of the most famous photoreceptor dyes is riboflavin, also known as vitamin B_2, which takes part in a lot of biochemical reactions as coenzyme.[1] Upon irradiation with blue light (440 nm) their redox power is dramatically increased: The reduction potential for the two electron reduction is about -200 mV.[2] This can be used for oxidative chemistry:[3] The reduced flavin is simply reoxidized by air.

When air is excluded new reduction pathways are enabled: The reduced flavin can be excited *via* UV-light which raises the reduction power enormously. We present our first results investigating organic reactions with reduced flavins.

Research supports: DFG: GRK 1626 – Chemical Photocatalysis.

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Keywords: *Photocatalysis; Flavin; Reduction;*

P-0452

NEW C-BRIDGED N-HETEROCYCLES AS CHIRAL LIGANDS AND FOR COPPER DIOXYGEN COMPLEXES

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New *C*-bridged *N*-heterocycles as chiral ligands: The concept of *C*2-symmetry has proved to be invaluable for asymmetric catalysis. Among the vast number of ligands known, the most successful ones such as the binaphthyls or the bisoxazolines contain a *C*2-symmetry axis, and only a few notable exceptions such as phosphinooxazolines or ferrocenyl ligands are equally effective chiral inductors.

As the fact that *C2*-symmetrical bisoxazolines are excellent ligands, we were interested in similar methylene-bridged *N*-heterocycles like bispiperidine or bistetrahydroquinoline as new chiral ligands. In comparison to the bisoxazoline nitrogen the bispiperidine-analogue nitrogen is electronic different due to its hybridization from which some differences in complexation properties can be expected. To study these new ligands we synthesized them, analyzed them and use them to prepare different complexes. After this they will test as asymmetric catalyst. Results of these studies will be presented on the poster.

Copper dioxygen complexes with some of these ligands: Copper is known as active centre of several redox active metalloproteins. Because of the ability of many copper enzymes to catalyse selective oxidations with air, one of the goals in bioinorganic chemistry currently is to model this functionality and to use such small molecular synthetic copper complexes as catalysts for selective oxidation reactions in the laboratory and in industry. To get such a model complex, oxygen is allowed to react under controlled conditions with a copper(I)-complex of the *N*-heterocyclic ligands. To study a couple of these model complexes, they were synthesized and characterized by using in this case some similar methylene-bridged *N*-heterocyclic ligands like bispiperidine or bisquinoline. Results of these studies will be presented on the poster.

Keywords: *N ligands; Asymmetric catalysis; copper; O-O activation;*

P-0453

SYNTHESIS AND OPTICAL PROPERTIES OF BIS(TERPYRIDINE)OLIGOTHIOPHENES AND RELATED METALLO-SUPRAMOLECULAR DYNAMERS

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Reversible linking of α,ω-functionalized oligomer molecules by noncovalent interactions or appropriately labile covalent or coordination bonds transforms the oligomers into constitutional-dynamic polymers, co called dynamers. Main advantages of dynamers are possibilities of additional modification (in order to tune or tailor their properties) or self-healing of the main chains by an exchange or reshuffling of their components. Ideal systems of this constitution can be repeatedly switched, in contrast to classical permanent polymers composed of irreversible macromolecules.

Novel, fully π-conjugated ditopic oligomers: α,ω-bis(terpyridine)oligothiophenes (bithiophenes and terthiophenes, unsubstituted, methyl- or hexyl- substituted), were synthesized via Pd-catalyzed organic cross-coupling reactions from monoterpyridine compounds. The obtained products were fully characterised and their optical properties (absorption and emission maxima, lifetimes of excited states and photoluminescence efficiency) are presented as function of their structure. Interaction of soluble compounds with Zn^{2+} ions were studied with absorption and emission spectroscopy. Metallo-supramolecular dynamers were obtained from the reaction of bis(terpyridine)oligothiophenes with Zn^{2+} salts and additional exchange of counterions.

On the basis of our results, we can draw several principal conclusions: (**i**) the wavelength of the longer-wavelength maximum of the oligomer absorption increases with oligothiophene linker prolongation and (**ii**) decreases with introduction of alkyl group onto thiophene ring, (**iii**) the emission maximum in photoluminescence spectra increases with conjugated chain prolongation. The lifetimes of excited states are relatively short (0.55–0.77 ns) and the photoluminescence emission quantum yields are 33–43% for bis-terpyridines with non-substituted oligothiophene linker and 12–23% for compounds with alkyl-substituted oligothiophene linker. Detailed characterization of metallo-supramolecular dynamers is currently underway in our laboratory.

Both π-conjugated oligomers as well as related supramolecular dynamers might be, after additional detailed study of their electronic properties in solution and solid phase suitable materials for light emitting devices or dye-sensitized solar cells.

Keywords: *C-C coupling; N-ligands; supramolecular chemistry; UV/Vis spectroscopy; fluorescence;*

P-0454

ASYMMETRIC DIELS-ALDER REACTION WITN NITROACRYLATE

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Diels-Alder reaction of nitropropenoates with various dienes constitutes one of the approaches to regioselectively substituted cyclohexenes. Interestingly, its enantioselective variant that would open a route to asymmetrically substituted cyclohexenes remains hitherto a rather unexplored area. Since there are numerous interesting compounds possessing chiral cyclohexene scaffold (e.g. Tamiflu,[1] carbasugars, etc), this method is of considerable synthetic interest. We focused on asymmetric Diels–Alder reaction of the nitroacrylate bearing chiral ester auxiliary group with 1-alkoxydienes. Although the formation up to eight possible stereoisomers could be expected as the result of the Diels-Alder reaction, only two of them were preferentially formed owing to structural features (steric and electronic) of both reactants[2]. Influence of reaction conditions on the stereoisomer ratio, and asymmetric induction will be discussed. In addition, further transformation of the obtained products into advanced synthetic building blocks and their application in organic synthesis will be presented as well.

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Keywords: *Asymmetric synthesis; Cycloaddition; Chiral auxiliaries;*

P-0455

MICHAEL ADDITIONS USING NITRO DERVIATES – A KEY STEP FOR THE SYNTHESIS OF INDOLE ALKALOIDS AND RELATED N-CONTAINING HETEROCYCLES

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The addition of compounds with an activated C-H bond to *α,β*-unsaturated molecules like esters, ketones or nitro-derivatives, e.g. the so called *Michael* acceptors, is a well known method for the formation of C-C single bonds.[1] *Michael* started in 1887 to describe the base catalyzed reaction of malonates with enones within a couple of publications.[2] Nowadays, nearly every 1,4-addition of a nucleophile to an activated double bond is called *Michael* addition.

Nitroalkenes are often used for the synthesis of functionalized amines by *Michael* addition and subsequent reduction of the nitro group. This way can be used for a broad variety of products, e. g. amino sugars, amino alkohols and diamines.3 Thus, nitroolefines are excellent *Michael* acceptors with only a neglectable tendency towards 1,2-addition and a strong anion stabilizing property of the nitro group.[2] The asymmetric *Michael* addition enables high enantioselectivities using simple, protonated triamine and diamine catalysts for the enantioselective addition of cyclic ketones to nitroalkenes.[4] Furthermore the cascade intermolecular *Michael* addition facilitates a salient feature using a Lewis acid catalyzed intermolecular *Michael* addition followed by a thermal induced intramolecular azide/internal alkyne 1,3-dipolar cycloaddition reaction in one pot.[5]

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P-0456

SELF-ASSEMBLING UNITS BASED ON PHYTOSTEROLS

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In past, bile acids have often been used in designing supramolecular structures. Recently, we have used selected phytosterols as elementary units for designing self-assembling systems. The first step of my investigation consisted in synthesizing hemiesters of sterols (e.g., stigmasterol, sitosterol or ergosterol), which were prepared by reacting anhydrides of dicarboxylic acids with appropriate phytosterols in dry pyridine and in a presence of the catalytic amount of DMAP. The yields of these esterification reactions varied from 49 % (branched anhydrides) to 93 %. These intermediate hemiesters were used for subsequent synthesis of conjugates with nitrogen containing compounds (e.g., esters of selected amino acids or other heterocyclic substances). Reactions were made in the dry dichloromethane, and DCC and DMAP were used as catalysts. The required amides were obtained with the yields exceeding 90 %.

Physico-chemical characteristics of the prepared conjugates were subjected to investigation. Their UV spectra were measured either in acetonitrile / water or ethanol/water (from 100% solvent to 100% water) systems. Only the solvent ratios changed, while the concentrations of the studied conjugates were always constant during the investigation. Changes in the intensity and/or position of the maximum absorbance in the UV spectra were recorded and evaluated. Self-assembly behavior of the studied compounds was indicated by non-linear dependence of the UV maximum absorbance on time and solvent ratios. Several substances have been proven to form gels reversibly in selected solvents, and at a given temperature.

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Keywords: *Steroids; Self-assembly; Amides; UV/Vis spectroscopy;*

P-0457

MIXED MATRIX MATERIALS BASED ON HYPERBRANCHED POLYIMIDE AND SILICA

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Linear aromatic polyimides show a very good overall stability from – 150 to 250 °C. In recent years, an increasing attention has been devoted to hyperbranched polyimides due to a possible connection of the advantages of polyimides with those of hyperbranched polymers. The important structural features of hyperbranched polymers are a highly branched structure, absence of chain entanglements and large number of terminal groups. Polyimides are especially employed in electronics, aircraft industry and as membranes in gas separations. They show high selectivity in gas separation but traditionally low gas fluxes. It has been reported that the permeability coefficients of some gases in the membrane prepared from a hyperbranched polyimide were 2 – 3.5 higher than those in the membrane prepared from a linear polyimide having similar chemical composition at the comparable selectivities. The incorporation of microporous/mesoporous materials into polyimides may further increase their permeability [1].

In this work, the mixed matrix materials based on the hyperbranched polyimide bearing amino end-groups (prepared from 4,4'-oxydiphthalic anhydride and 4,4',4''-triaminotriphenylmethane) and silica (up to 20 wt% of nano- or mesoporous particles) were prepared. 3-Glycidyloxypropyltrimethoxysilane was used as a coupling agent (its epoxy groups react with amino end-groups of the hyperbranched polyimide and alkoxy groups with silanol groups of the silica). The thickness of self-standing films was about 50 microns. The composition – (thermal, mechanical) property relationships of these materials were evaluated. The permeability coefficients of some gases were also determined. Their analysis has brought some fruitful results (e. g. a membrane containing 20 wt% of mesoporous silica bound to the polymer matrix shows about 150% increase in the oxygen flux in comparison with a pure hyperbranched polyimide membrane and the selectivity oxygen/nitrogen reaches up to 9).

Acknowledgement: *GA CR P106/12/0569*

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Keywords: *hyperbranched polyimide; silica; coupling agent; mixed matrix material;*

P-0458

BIOACTIVE HETEROCYCLES – INTERMEDIATES OF A NATURAL PRODUCT INSPIRED SYNTHESIS AS POTENTIAL ANTIBACTERIAL LEAD COMPOUNDS

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Since penicillin was introduced into the clinical setting in the 1940s, antibiotic resistance has emerged very rapidly. As subsequent generations of this class of antibiotics contained a similar molecular scaffold which act upon similar cellular targets within the bacteria, the development of further resistance have been accelerated.[1]

In recent drug discovery processes, early combinatorial approaches have not delivered the expected results, and no new chemical entities from *de novo* combinatorial chemistry for antibacterial compounds have been reported; it is now thought that the diversity of the libraries was too limited, having been prepared from narrowly focused commercially available starting materials, principally coupled by amide bond formation. The library thus formed is inadequate to populate a sufficiently large area of chemical space to provide the required hits.[2, 3]

We are interested in the development of novel antibacterial compounds, and have used biologically active natural products as starting points for potential lead compounds in the drug discovery process, since they are evolutionarily selected for binding to specific protein domains, possibly providing a ‘privileged’ structural framework.[4]

Herein, we describe the synthesis of heterocycles based on the natural product (-)-Pramanicin, starting from known enantiopure compounds derived from pyroglutamic acid and $_{\text{L}}$-Serine. These analogues have been assessed by bioassay, and activities have been correlated with physicochemical parameters calculated using a software (MARVIN 5.3.8), in order to assess their potential for application as lead compounds.

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Keywords: *Drug discovery; Heterocycles; Antibiotics;*

P-0459

ASYMMETRIC DIRECT ALDOL REACTION IN WATER ORGANOCATALYSED BY RECYCLABLE AND HETEROGENEOUS CHITOSAN AEROGELS

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The development of heterogeneous catalytic systems for fine chemical synthesis has become a major area of research. The ability to use heterogeneous catalysts in the liquid phase can aid considerably in the separation, recovery and reuse of catalysts. It can afford clean separation of products from the crude thus making a major impact on the environment performance of a synthesis. Chitosan derived by deacetylation of chitin (biopolymer obtained from sea crustaceans) can be considered as a natural polyamine.

The lack of literature reports dealing with the heterogeneous asymmetric organocatalysis displayed by polysaccharides prompted us to undertake a detailed study of the chitosan potential in this new frontier area of organocatalytic reactions. Accordingly, to evaluate the putative chitosan catalytic activity, the direct aldol reaction, one of the most important carbon-carbon bond forming reactions, was investigated in water without any organic co solvent, by using supercritical CO_2 dried chitosan as the catalyst. Indeed aerogel formulation of chitosan affords high surface area materials (up to 350 $m^2.g^{-1}$) with high accessibility to the functional groups (up to 5.2 $mmol.g^{-1}$ NH_2).[1] Initial tests were performed in the reaction between p-nitrobenzaldehyde and cyclohexanone aimed at establishing the optimized reaction conditions. Then, aerogel microspheres of chitosan have successfully catalyzed the asymmetric aldol reaction in water, providing the products in high yields, with good stereoselectivity (up to 93 % ee) and recyclability (up to 4 runs). Yields were favourably affected by additives such as 2,4-dinitrophenol and stearic acid. We have developed the first direct asymmetric aldol reaction that can be performed in water using chitosan as heterogeneous organocatalyst.[2] The simple and environmental friendly experimental procedure and the recycling of the catalytic systems highlight good assets of this protocol.

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Keywords: *Natural Products; Biomass; Enantioselectivity; Green chemistry;*

P-0460

FLUORINATED ORGANOCATALYSTS FOR THE ENANTIOSELECTIVE EPOXIDATION OF ENALS: MOLECULAR PRE-ORGANISATION BY THE FLUORINE-IMINIUM ION GAUCHE EFFECT

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The fluorine-iminium ion *gauche* effect,[1, 2] and its strategic use in the design of small molecule organo-catalysts that undergo conformational changes in response to substrate binding will be described. The condensation of a secondary β-fluoroamine with an α,β-unsaturated aldehyde reversibly generates a β-fluoroiminium salt as a consequence of stabilizing hyperconjugative interactions (e.g. σ_{C-H}?σ^*_{C-F})[1] as well as electrostatic/charge dipole interactions[3] with the electropositive center (e.g. $F^{\delta-}$-C_β-C_α-N^+). Introducing additional structural features leading to stabilizing (e.g. π-stacking or C-H-π interactions) or destabilizing interactions helps discriminate between the two possible *gauche* conformations. Consequently, substituents attached to the fluorine-bearing carbon can be predictably positioned in an area of molecular space and, in the case of enantioselective organocatalysis, exploited as shielding groups to direct incoming nucleophiles to one of two faces of a planar electrophile. The β-fluoroamine (*S*)-2-(fluoro diphenylmethyl)-pyrrolidine[4] is an effective catalyst for the Weitz-Scheffer epoxidation of alpha-beta-unsaturated aldehydes. A process of structural editing[5] has revealed that the efficiency of this catalyst is due to the (fluorodiphenyl)methyl group when it is embedded in a β-fluoroiminium motif. Furthermore the epoxidation of challenging cyclic α,β-disubstituted, β,β-disubstituted and α,β,β-trisubstituted enals[5] catalysed by (*S*)-2-(fluoro diphenylmethyl)-pyrrolidine proceeded with excellent levels of enantiocontrol (up to 98% *ee*).

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Keywords: *Conformation analysis; Enantioselectivity; Fluorine;*

P-0461

COMPARATIVE STUDY OF ENOLETHERS WITH R-HYDRAZINES IN EXPERIMENTS AND KINETICS

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Selected enolethers[1, 2] provided with R-hydrazines as binucleophiles (R = H, methyl, acetyl, phenyl) products of vinylic nucleohilic substitution reaction at room temperature by using of appropriate solvents. There were observed cyclization products by addition-elimination step at higher temperature opposite to the room tepmperature. On these sytems were realized kinetic studies for same conditions as for experiments. Reactions took place in ultra rapidly, reaction run by pseudo – first order. These fact gave us valuable results in the kinetic study of these isoelectronic systems[3].

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Keywords: *enolethers; vinylic nucleophilic substitution reaction; pseudo-first order;*

P-0462

MG/AL HYDROTALCITES: STRUCTURAL AND CATALYTIC BEHAVIOUR IN HETEROGENEOUS CYANOETHYLATION

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The preparation, characterization and catalytic behavior of hydrotalcites (LDH), mixed oxides obtained via LDH thermally decomposition and reconstructed LDH by means of memory effect were extensively reported in the literature[1–3]. LDH is considered an ionic lamellar class of base solid catalysts and there are many evidences on their efficiency in various heterogeneous basic reactions.

In this study we report the preparation of Mg/Al LDH with molar ratio 3, by co-precipitation of Mg and Al nitrated solutions with Na_2CO_3 and NaOH at pH = 10. The solids were thermally decomposed at 460°C in air atmosphere in order to obtain mixed oxides which were then hydrated with bi-distilated water for the reconstruction of the LDH structure. The solids obtained were characterized using *in-/ex-situ* techniques such as: XRD, DRIFTS, CO_2-TPD, N_2 adsorption-desorption isotherms. The catalytic activity of the solids was evaluated in cyanoethylation reaction between different alcohols (methanol, ethanol, propanol) and nitriles (acrylonitrile, crotonitrile, cinnamyl nitrile). All these reactions arising with a higher selectivity in the desired product. No by-products were detected by means of GS-MS chromatography and ^{1}H-NMR. As an example, the conversion of nitrile with ethanol was 98% with acrylonitrile and around 30% with crotonitrile and cinnamyl nitrile using reconstructed samples.

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Keywords: *base; solid catalysts; cyanoethylation;*

P-0463

SYNTHESIS OF PYRIMIDO[4,5-B]INDOLE RIBONUCLEOSIDES BEARING (HET)ARYL GROUPS AT POSITIONS 4 AND 6

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Introduction: 7-Deazapurine nucleosides bearing hetaryl group in position 6 and H, F or Cl atom at position 7 showed cytostatic activity against multiple cell lines. Furyl and thienyl derivatives were the most active compounds.[1] Based on previous results, goal of this work was the synthesis of new type of annulated deazapurine derivatives bearing hetaryl group for biological testing.

Results and discussion: The synthesis of 4,6-dichloro-9*H*--pyrimido[4,5-*b*]indole and its ribosylation to protected ribonucleoside intermediate has been developed starting from 2,4-dichloronitrobenzene. This five-step synthesis (nucleofilic substitution, reduction, heterocyclization, substitution and glycosylation) has been optimized for tens gram scale with only one final column chromatography and excellent overall yield 30 %.

A series of target ribonucleosides bearing aryl or hetaryl group at position 4 of pyrimidine ring has been prepared by regioselective Pd-catalyzed Suzuki or Stille cross-coupling reactions[1] of protected nucleoside in good yields. Final deprotection under the Zemplen conditions using NaOMe in methanol led to free nucleosides in 70 - 90 % yields. Further arylation at position 6 is possible only under modified conditions using Buchwald ligands in good yields (62-79 %). Final deprotection furnished desired free nucleosides in 90 % yields. Title 4,6-disubstituted derivatives were tested for biological activities.

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Keywords: *pyrimido[4,5-b]indole ribonucleosides; palladium cytalysed cross-coupling;*

P-0464

FROM BIFUNCTIONAL LIGANDS TO A DIVERSITY OF HOMO- AND HETEROMETALLIC COMPLEXES

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In metallo-supramolecular self-assembly, ligands containing different coordination motifs are interesting building blocks which can be used for a large variety of different purposes like hierarchical self-assembly or self-sorting. Inspired by these possibilities, a series of four ligands was designed, which contain one 2,2'-bipyridine coordination site that is substituted in 4,4'- or 5,5'-position, respectively, with two pyridine binding moieties. Additionally, the position of the nitrogen atoms in the pyridine moieties is varied.

The combination of these ligands with suitable metal centers with different coordination numbers and coordination geometries results in the formation of different metallo-supramolecular structures. Discrete metallo-supramolecular complexes are obtainable as well as metal-organic frameworks. When the ligands are combined with a suitable combination of two or more different metal centers also the formation of heterometallic structures is observed.

For example, the combination of the ligands under study with two equivalents of *cis*-blocked square-planar $[Pd(en)](NO_3)_2$ results in the formation of M_2L complexes using the 4,4'-substituted ligands or M_4L_2 complexes for the 5,5'-substituted ligands (M = metal center; L = ligand), respectively.

When the 4,4'-substituted ligands are combined with square-planar $[Pd(CH_3CN)_4](BF_4)_2$, the formation of metallo-supramolecular macrocycles is observed. For example, the ligand containing two 3-pyridine moieties results in the exclusive formation of M_4L_4macrocycles, wherein one Pd(II) ion is coordinated by one 2,2'-bipyridine unit and two pyridine units of the next ligand. Thus, the M_4L_4 complexes are unidirectional, which would result in chiral complexes, when those complexes are adsorbed on a proper surface.

By a combination of the ligands with 1/3 eq. of an iron(II) salt ML_3 complexes can be achieved, which are interesting precursors for further self-assembly reactions. Mixing these ML_3 complexes with other metal centers leads for example to the formation of heterometallic metal-organic frameworks.

On the poster we present some of the structures described above.

Keywords: *supramolecular chemistry; metal complexes; heterometallic complexes; self-assembly; functional ligands;*

P-0465

ASYMMETRIC REDUCTION OF PROCHIRAL KETONES WITH BORANE USING CHIRAL BETA-HYDROXAMIDES DERIVED FROM NAPHTHOIC ACID AND CHIRAL AMINO ALCOHOLS AS CATALYSTS

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Enantiopure oxazaborolidine-catalyzed borane reduction of prochiral ketones is one of the most important methods to prepare optically pure secondary alcohols[1, 2]. Such alcohols are important intermediates for the synthesis of various organic compounds including liquid crystalline materials as well as biologically active compounds[3]. The pioneering work of Itsuno and coworkers was developed by Corey and Link, and called as CBS (named after Corey, Bakshi, and Shibata) reduction. The study of catalysts derived from chiral oxazaborolidine has become one of the most active research fields[4].

A series of β-hydroxyamides were synthesized from 3-hydroxy-2-naphthoic acid and chiral amino alcohols. Their catalytic activity in asymmetric borane reduction of prochiral ketones was investigated. After the fine optimization of solvent, temperature, amount of borane complex, and the length of catalyst generation period, good to excellent yields (up to 99 %) and enantioselectivity (up to 96 %) has been achieved.

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Keywords: *beta-hydroxamides; asymmetric reduction; borane reduction; prochiral ketone;*

P-0466

KINETIC RESOLUTION OF 4-HYDROXY-2-CYCLOPENTENONE DERIVATIVES BY PD-CATALYZED ALLYLIC ALKYLATION AND APPLICATION IN SYNTHESIS OF CARBOCYCLIC NUCLEOSIDES

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Today there is an increasing interest in methods applying renewable materials as the source of chemical building blocks. Furan derivatives like furfuryl alcohol are mainly produced from agricultural waste and consequently come not into conflict with food production.[1] They offer interesting possibilities for chemical transformations like the rearrangement of furfuryl alcohol to 4-hydroxy-2-cyclopentenone. For this reaction a continuous flow process was developed in our group giving the racemic product in high yield.[2] As this substance was inexpensively available in our group, different enantiomerically pure 4-substituted 2-cyclopentenones, which are useful chiral building blocks for synthesis of many important compounds,[3] have been synthesized. This was accomplished by kinetic resolution of 4-(*tert*-butoxycarbonyloxy)-2-cyclopentenone, which was obtained from the free alcohol by simple Boc-protection, with Pd-catalyzed asymmetric allylic alkylation using a chiral ligand. Various oxygen-, nitrogen- and sulfur-nucleophiles have been employed in this reaction giving excellent yields and selectivities. An application for the kinetic resolution was found in the synthesis of carbocyclic nucleosides, which show interesting biological activity. One main obstacle in their synthesis is the use of expensive enantiomerically pure starting materials or the introduction of the stereochemical information when using racemic compounds.[4] Our method overcomes this problem by starting from racemic 4-(*tert*-butoxycarbonyloxy)-2--cyclopentenone and 6-chloropurine as nucleophile in the kinetic resolution, which gives the 4-substituted product in high yields and with excellent enantiomeric excesses. This product presents an important intermediate in the synthesis of certain carbocyclic nucleosides.[5]

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Keywords: *Asymmetric catalysis; Enantioselectivity; Kinetic resolution; Palladium; Renewable Resources;*

P-0467

SWITCHING MOLECULES ON SURFACES – A PLATFORM APPROACH

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Azobenzenes and other photochromic molecules have gained great attention as molecular switches. In this project we are developing methods to attach azobenzene derivatives to single crystalline Au(111) surfaces.

To minimize the electronic coupling of the azobenzene with the gold surface and to prevent steric interaction with neighbouring molecules the azobenzene units have to be anchored in an upright position with a well defined orientation and distance to the surface and to each other. This approach should provide higher quantum yields for photochemical switching (trans to cis and cis to trans) then azobenzenes physisorbed flat on the surface. Moreover with polarized light it should be possible to control the switching direction.

A promising method to achieve the above mentioned properties is the use of TATA (triazatriangulenium) and TOTA (trioxatriangulenium) as platforms. Azobenzene molecules can be covalently attached to the central carbon atom and are therefore perpendicular to the plane of the platform.[1]

Both the unfunctionalized and functionalized platforms form hexagonally ordered self assembled monolayers on Au(111) surfaces.[2, 3, 4]

More advanced lateral structures will be attempted by substitution of the platforms with hydrogen-bond donor and acceptor domains. Via supramolecular interactions the platforms should form well-defined and highly ordered mixed monolayers. Using functionalized platforms with different functional groups attached to the central carbon atom, also control of vertical growth could be possible.

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Keywords: *platform; gold surface; functionalized adlayers;*

P-0468

REGIOSELECTIVE CYCLOPOLYMERIZATION OF 1,7-OCTADIYNES

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The cyclopolymerization of 1,6-heptadiynes via olefin metathesis is a powerful method for synthesizing soluble, conjugated polyacetylene-type polymers[1]. Using designed Schrock-type initiators, the regioselective cyclopolymerization of 1,6-heptadiynes provides either five- or six-membered repeat units via a- or b- addition, respectively[2]. With 1,6-heptadiynes, b- addition leads to the formation of six-membered repeat units and few examples for selective b- addition have been reported[3]. Here we report on the regioselective cyclopolymerization of 1,7-octadiynes[4]. In order to elucidate on the structure of the resulting polymers, we synthesized the diastereomeric 4,5-diethoxycarbonyl-1,7-octadiynes from which the pure diastereomers were obtained by Soxhlet extraction in $CHCl_3$. Using the concept of "small alkoxides" developed by Schrock et al.[5], all monomers were cyclopolymerized with a series of different Schrock-type initiators, varying the size of the alkoxide ligands. As a result, poly(1,7-octadiyne)s with a high content of six-membered repeat units (> 90 %) were obtained. Both the structure of the polymers and the regioselectivity of insertion were confirmed by comparing the ^{13}C-NMR shifts of model compounds with those of the corresponding polymer. The living character of the polymerization was demonstrated by kinetic studies and end group analysis via MALDI-ToF MS. Finally, diblock copolymers were prepared from an 1,7-octadiyne and a 1,6-heptadiyne.

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Keywords: *Metathesis; Polymerization; Catalysis; Molybdenum; Kinetics;*

P-0469

METALLO- AND PHOTO- SWITCHED DYNAMIC NETWORKS

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Hydrazones may be considered as tools, used in constitutional dynamic chemistry (CDC), to control the constitution of dynamic networks. They exhibit double-dynamic properties [1]: **a**) constitutional dynamics, by exchange of hydrazone bounds; **b**) configurational dynamics, by metal coordination and photochemical cis-trans isomerization.

A dynamic network based on hydrazones has been designed to respond differently to two types of stimulation: physical (light irradiation) and chemical (addition of a metal cation) thereby undergoing adaptation of their constituents via component exchange and selection. These switched dynamic networks offer the prospect of long term information storage, training of the system to recognize different effectors and formation of an ecological niche.

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Keywords: *Combinatorial Chemistry; Supramolecular Chemistry; Hydrazones;*

P-0470

AZONIA CATIONS BY RING-CLOSING METATHESIS

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Quinolizinium derivatives[1] have proven useful in some applications such as cyanine dyes and highly fluorescent compounds used as probes for the detection of biomolecules. These compounds also show some relevant biological activities and the quinolizinium system is present in a variety of natural alkaloids such as coralyne and the family of berberines. Other significant alkaloids such as sempervirine, flavopereirine, neooxygambirtannine and afrocurarine inter alia are based on an indolo[2,3-a]quinolizinium heterocyclic system.

Recently, our group reported the ring–closing metathesis (RCM) reaction of a new type of azinium azadiene, which allowed a novel approach to dihydroquinolizinium and quinolizinium cations from pyridinium salts in good overall yields under mild reaction conditions.[2, 3] The success of the RCM reactions involving this class of charged diene, particularly those based on 2-alkenyl-
-1-vinylpyridinium substrates, led us to explore the synthesis of systems from the appropriate azinium salts.

In this communication we will report our results to access to benzo-, dibenzo-, naphtho-, aza- and indolo[2,3-a]quinolizinium derivatives using different approaches based on a RCM as key reaction.

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Keywords: *Hetocycles; Cations; Metathesis; synthetic methods;*

P-0471

KINETIC INVESTIGATION OF A CINCHONA BASED ORGANOCATALYTIC MICHAEL ADDITION

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Organocatalysts represent a powerful tool for creation of C-C bond, in particular, many new bifunctional organocatalysts were described for enantioselective Michael addition, in the past decade. Most of these researches target new substrate applications. On the other hand, we focus herein on the kinetics of an organocatalized Michael addition.

We studied the addition of acetylacetone and β-nitrostyrene using a cinchona based squaramide catalyst in order to understand better the mechanism of the catalytic reaction and to determine the rate-limiting steps. Kinetic studies were carried out under synthetically relevant conditions and the reactions were followed by in situ IR measurement, and were confirmed with ^{1}H-NMR spectroscopy.

Based on kinetic analysis we conclude, that the reaction rate shows linear dependence on the catalyst concentration. The order of β-nitrostyrene was found to be around one at low initial concentration (up to 0.6 mol/dm^3), while at higher initial concentration, we found high reaction rate and product inhibition. The significant product inhibition was also confirmed by addition of the product at the beginning of the reaction: we observed a dramatic rate decrease. Surprisingly, the reaction rate does not clearly correlate with acetylacetone concentration, the order in this reactant is lower than one. We suggest competitive binding of acetylacetone and product to the active site of the catalyst. We also confirmed this assumption by investigation of catalyst-substrate complexes by NMR spectroscopy. Additionally, the effect of temperature was also studied, and the activation energy of the reaction was calculated.

On the poster we shall present all the detailed kinetic studies and the proposed catalytic cycle describing the reaction mechanism.

Keywords: *Organocatalysis; Kinetics; Michael addition;*

P-0472

NANO-PALLADIUM ON AMINO-FUNCTIONALIZED MESOCELLULAR FOAM: AN EFFICIENT CATALYST FOR TRANSFER HYDROGENATIONS AND SUZUKI REACTIONS

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Nanoparticles have recently attracted an increasing interest because of their unique properties and numerous applications in a variety of fields, including electronics, energy technology, optics, magnetism, and chemistry. In chemistry, heterogenous catalysts based on transition-metal nanoparticles have shown to be efficient and selective for a wide range of organic transformations under mild conditions. Furthermore, heterogeneous catalysts allow for simpler separation and recycling of catalyst compared to homogeneous counterparts. This solves many practical problems associated with industrial-scale production of chemicals and pharmaceuticals, where metal impurities in the final products can possess an issue of major concern.

Among the many types of heterogeneous catalysts developed so far, those based on palladium have in general exhibited highest activity and selectivity. In our group, we have recently developed a heterogeneous catalyst based on Pd nanoparticles immobilized on siliceous mesocellular foam (MCF). Here we report on the applications of the Pd nanocatalyst in Suzuki cross-coupling reactions and transfer hydrogenations of alkenes are described. The catalyst showed to be highly efficient for both transformations, resulting in (**i**) facile coupling of a wide range of aryl halides with various boronic acids in high yields and (**ii**) chemoselective reduction of variety alkenes employing 1-methyl-1,4-cyclohexadiene as hydrogen donor. Moreover, the catalyst can be recycled several times without any significant decrease in activity or leaching of metal into solution.

Keywords: *Heterogeneous Catalysis; Cross-coupling; Hydrogenation; Green Chemistry; Nanoparticles;*

P-0473

RECENT DEVELOPMENTS IN HOMOGENEOUS GOLD(I) CATALYSIS

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For more than two decades gold(I) has been used to activate carbon-carbon multi-bonds towards nucleophilic attack and thus has induced the formation of carbon-hetero atom bond.[1] The role normally ascribed to gold(I) in such reactions is that of an activator of carbon-carbon multi-bonds by pi-coordination. However, recently a new type of homogeneous gold catalysis has been added to the repertoire – namely that of gold participating in two distinct roles through dual sigma/pi activation.[2, 3] This presentation will focus on some of the newest developments within the field of homogeneous gold-catalyzed reactions forming carbon-carbon bonds or carbon-heteroatom bonds.

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Keywords: *Gold; Catalysis; Alkynes; Polycycles; Heterocycles;*

P-0474

A GOLD-CATALYZED ENTRY TO HETEROCYCLIC SPIRO COMPOUNDS

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Many natural products contain spiroacetals as characteristicstructure element. Synthesis methods for the most common [O,O]-spiroacetals arewell known, e.g. under Lewis- or Bronsted-acid catalysis.[1, 2] Otherheterocyclic spiro compounds have been relegated to a niche existence.

As a carbophilic Lewis-acid, gold has the ability toactivate alkenes and alkynes for nucleophilic attack to form C-C-, C-O-, C-N-or C-S-bonds.[3] The obvious advantages of gold catalysis are mildreaction conditions at oftentimes room temperature, tolerance against differentfunctional groups and its low toxicity, which is useful for the application inthe synthesis of drugs.

Previously, we have shown that tetrahydrofuranylethers are accessible by gold-catalyzed tandemcycloisomerization--hydroalkoxylation of homopropargylic alcohols.[4] We now disclose a new access to [N,O]-spiroacetals by cyclization ofaminoalkynols in the presence of a gold catalyst.[5] This methodtolerates various substituents and protecting groups and can be used to accessspiroacetals with five- or six-membered rings. By changing the nucleophilicpositions (eg. thiols or esters), this method provides a new access to a widerange of interesting heterocyclic spiro compounds.

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Keywords: *Spiro compounds; Gold; Cyclization; Heterocycles; Homogeneous catalysis;*

P-0475

ISOTHERMAL CALORIMETRIC TITRATIONS ON CHARGE-ASSISTED HALOGEN BONDS: ROLE OF ENTROPY, COUNTERIONS, SOLVENT AND TEMPERATURE

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Halogen bonds (XBs) are non-covalent interactions between terminal halogen bonds in compounds R-X (X = Cl, Br, I) and a Lewis base (LB), analogous to hydrogen bonds (HBs).[1] Due to their high directionality, the main application of XBs so far has been in *crystal engineering*, and as a consequence, most determinations of the interaction strength of halogen bonds have been carried out in the solid state.[2]

Though well-established in solution (and in the gas phase), systematic studies of XB-strengths in liquids have been rare. Using isothermal titration calorimetry (ITC), we have carried out extensive investigations on the interaction between cationic bidentate halogen bond donors (R-X) and halides (LBs) in different solvents and at different temperatures in order to gain insight into the role of various factors on halogen bond strength in solution.[3] Several derivatives of bis(haloimidazolium) compounds were used as XB-donors. The data collected in these experiments is intended to aid the rational design of halogen bond donors as well as the development of XB-based applications in solution. In all cases examined, the entropic contribution to the overall free energy was found to be of major significance. The binding affinities became slightly stronger with higher temperatures, while showing little dependency on the weakly-coordinating counter-anions of the halogen-bond donors. We also noted a marked influence of different solvents on the interaction strength.

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Keywords: *halogens; non-covalent interactions; thermodynamics;*

P-0476

ALIPHATIC POLYKETONES OBTAINED FROM DIMETHYLKETENE AND ETHYLKETENE

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Ketenes are derivatives of carboxylic acids which contains two consecutive double bonds (C=C=O).[1, 2] By ionic polymerization, and assuming a suitable choice of initiator and solvent, ketenes can lead to polyketone, polyester or polyacetal. Previous works in our laboratory showed that a film made of the dimethylketene-based polyketone present excellent gas barrier properties (ex: oxygen, water vapor and carbon dioxide) even in the presence of humidity, enabling this material to compete with the compounds currently used in the food packaging industry.

The purpose of my thesis is to elaborate new ketene-based aliphatic polyketones, using the several years experience gained in this field by the laboratory. Indeed, a major drawback of aliphatic polyketones is their poor processability. The introduction of defects in the macromolecular chains should decrease the crystallinity of the polymer and thus make easier its moulding. Firstly, the copolymerization involving dimethylketene and ethylketene in different proportions was carried out in toluene at –78°C, by using $AlBr_3$ as Lewis acid initiator, aiming at obtaining a statistical copolymer. Secondly, the polymerization of dimethylketene was tested using carbocation initiators, generated in situ by reacting chlorinated or brominated reactants or polymers with a Lewis acid in a Friedel-Craft process, to target block or star-shaped polyketones.

The composition of all the obtained polymers was determined by ^1H, ^{13}C NMR and FTIR, and the thermal properties were more particularly analyzed (RX, TGA, DSC).

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Keywords: *Carbocations; Polymerization; Polymers;*

P-0477

CATALYTIC CYCLIZATION AND ANNULATION REACTIONS OF AMINOCYCLOPROPANES

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Carbo- and hetero-cycles are omnipresent in bioactive natural and synthetic compounds. Consequently, the development of new cyclization or annulation methods for their synthesis is an important field of research in organic chemistry. In this context, donor acceptor-substituted cyclopropanes have been extensively used as precursors of reactive intermediates in cyclization and annulation reactions.[1–2]

Nevertheless, the use of aminocyclopropanes is still underdeveloped, despite the importance of nitrogen-based functional groups in bioactive molecules. In 2010, we have reported the first highly regioselective cyclizations of aminocyclopropanes onto indole heterocycles for the synthesis of natural alkaloids.[3]

Herein, we report the first Lewis acid-catalyzed [3+2] annulation reactions of aminocyclopropanes.[4–6] The reaction worked for olefins, aldehydes and ketones as partners. Key for success was the modulation of the push-pull properties of the substituents on the aminocyclopropane, with the optimum being met for phthalimide as donor and a diester as acceptor. In the case of olefins, the reaction is both stereospecific in relation to the configuration of the double bond and enantiospecific, giving access to enantiopure cyclopentylamines in high yields.[4] On the other hand, the reaction with aldehydes and ketones gives access to aminotetrahydrofurans, which constitute the core of DNA and RNA.[5–6] Current efforts in our laboratory focus on the transformation of the obtained products into bioactive compounds, as well as in the development of catalytic asymmetric methods.

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Keywords: *Annulation; Cyclization; Synthetic methods; Asymmetric synthesis; Alkaloids;*

P-0478

HYDROGENATION OF ALKENES AND ALKYNES WITH CATALYTIC IRON(0) PARTICLES

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Transition metal-catalyzed hydrogenations of alkenes and alkynes are among the most important synthetic transformations with numerous lab-scale and technical applications to the synthesis of fine chemicals, pharmaceuticals, natural products, the processing of vegetable oils and fatty acids, and in petrochemical conversions.

Over the past decades, iron catalysts have evolved as an attractive alternative to precious and toxic catalyst systems. Recently, several groups reported on nanoparticulate iron catalysts in reductions of carbonyl compounds, olefins, and alkynes.[1] As part of our program directed at the utilization of cheap iron catalysts for the synthesis and manipulation of fine chemicals,[2] we also became interested in the development of a practical and sustainable alternative to established Raney-Nickel-type catalysts.

We wish to report on a hydrogenation protocol that combines the economical and environmental benefits of iron as cheap and non-toxic catalyst metal with the operational simplicity of a heterogeneous process.

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Keywords: *Hydrogenation; Catalysis; Iron;*

P-0479

THE SYNTHESIS OF SUBSTITUTED TRIAZINES AS POTENTIAL SYNTHETIC AUXIN HERBICIDES

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Herbicides that act by mimicking the plant hormone auxin (indole acetic acid) have been known and used for 70 years. However, only in the last decade has the molecular mechanism of action of these compounds begun to be understood. In parallel with this increased knowledge a number of new herbicides of this class have been launched or entered development. These compounds have structures based on a pyridine and pyrimidine core, but there are no reports of synthetic auxins based on triazines.

We will describe our work to explore the potential of compounds with a 1,3,5-triazine core to act as synthetic auxins. Aspects of the design of the compounds will be discussed, as will a number of synthetic approaches to the desired targets and the biological results obtained.

Keywords: *triazine; herbicide; auxin;*

P-0480

POLYAMINE CONJUGATES OF SELECTED STEROLS: FROM DESIGN TO ANTIMICROBIAL AND CYTOTOXICITY TESTS

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Several new polyamine conjugates with stigmasterol and sitosterol were synthesized and subjected to basic antimicrobial and cytotoxicity tests. Selected sterols were transformed into their hemiesters with short-chained dicarboxylic acid anhydrides. The free carboxylic functionality of the sterol hemiesters was activated and then allowed to react with *N*-protected polyamines to form their amide conjugates. Finally, the *N*-protecting groups were removed affording the target products, for which their physico-chemical characteristics were calculated and compared with the Lipinski[1] and Ghose[2] rules. The conjugates derived from spermine displayed considerable antimicrobial activity on *Staphylococcus aureus*, a gram-positive bacterium at low concentration (50 mg.mL^{-1}), while these compounds were inactive towards several gram-negative bacteria. The cytotoxic activity was tested on cells of human T-lymphoblastic leukemia, breast adenocarcinoma, cervical cancer, and also on normal human fibroblasts, and the results will be presented in the IC-50 values indicating the lethal effect of the tested compound to 50 % of the tumor cells.

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Keywords: *conjugation; steroids; amides; antifungal agents; antitumor agents;*

P-0481

A GLYCOPOLYMERIC PT(II) CARRIER: SYNTHESIS AND IT'S INDUCTION OF APOPTOSIS IN RESISTANT CANCER CELLS

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The development of anti-cancer drugs overcoming resistance towards common cytostatics is one challenge in cancer research, in particular for Pt-based drugs.[1] Compounds that actively accumulate inside afflicted tissues and organs can be obtained by introduction of targeting moieties that specifically interact with cells or the usage of polymer vehicles, taking advantage of the enhanced permeability and retention effect in tumor vasculature.[2] Platinum-polymer complexes, dendrimers, micelles and micro-particulates are discussed in the current literature.[3] The therapeutic efficacy of the drug is increased, mechanisms of resistance are circumvented and the overall toxic side-effects reduced.

We present the synthesis of the first Pt^{II}-carrying glycopolymer with promising anti-cancer activities against resistant leukemia cells.

The materials synergizes the properties of glycopolymers and square-planar Pt^{II} complexes: Glycopolymers have found, for instance, applications in clinical diagnostics, targeted drug delivery, for affinity separations and bioassays.[4] Sugar moieties on polymeric backbones may act as cell-type specific ligands for a broad spectrum of protein receptors, providing macromolecules with targeting properties.[5] Terpyridine ligands are effective complexing units for transition metal ions leading to therapeutic agents or diagnostic tracers.[6] Since square-planar Pt^{II}-terpyridine complexes show high cytotoxicities due to DNA-intercalation,[7] they were choosen to prepare the glycopolymer with potential antitumor activity.

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Keywords: *Polymerization; Platinum; Cancer; Supramolecular Chemistry; Glycoconjugates;*

P-0482

INDUCED CHARGE EFFECT OF CO(II) IONS ON THE CONFORMATION OF A LIGAND-FUNCTIONLIZED COPOLYMER

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Poly(alkyl methacrylate) copolymers embedding bidentate 2-(1*H*-1,2,3-triazol-4-yl)pyridine (trzpy) chelating units as comonomer in the side chains were synthesized by controlled radical addition-fragmentation transfer (RAFT) polymerization. The RAFT polymerization technique led to well-defined copolymers as confirmed by ^{1}H NMR spectroscopy, size exclusion chromatography coupled with a photodiode array detector (SEC-PDA) and UV/vis titration experiments. The free trzpy units were complexed by Fe^{II} and Co^{II} ions, and the coordination behavior in solution was studied extensively by utilizing UV-vis and viscosity titration experiments as well as detailed analytical ultracentrifugation (AUC) investigations. Both metal salts showed a cross-linking ability in concentrated solution ($c > 10$ mg?mL^{-1}), whereby in the case of Co^{II} a highly viscous fluid was observed. Complexation of the polymer chains was observed, which resulted in characteristic UV-vis absorption bands and an increase in the solution viscosity. Addition of a solid coordinating ligand, such as *N*-(2-hydroxyethyl)-ethylenediamine triacetate (HEEDTA), resulted in a quantitative decomplexation. In a concentrated polymer acetone solution an exponential increase of the dynamic viscosity was observed after adding Co^{II} ions upon intermolecular cross-linking of the macromolecule chains. Furthermore, the intramolecular complexation with Co^{II} ions was studied in highly diluted acetone solution of the trzpy-containing copolymer by means of different analytical ultracentrifugation experiments. By the addition of a small amount of Co^{II} ions a significant decrease of the intrinsic sedimentation coefficient was observed, which could be explained by the elongation of the individual polymer coils upon the electrostatic repulsion of the coordinated Co^{II} ions.

Keywords: *Copolymerization; Supramolecular Chemistry; Analytical methods; Conformation analysis;*

P-0483

FORMATION OF 1,3-DIOXOLANES FROM EPOXIDES AND KETONES/ALDEHYDES USING $ZN(OTF)_2$ AS A CATALYST

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1,3-dioxolanes are important chemical raw materials, which can be used to synthesize steroids and carbohydrates, serve as the intermediates to protect carbonyl groups or diols. Besides, some 1,3-dioxolanes are used as solvent in chemical reactions. In the recent year, some 1,3-dioxolanes are found to have special flavor and are used in food and tobacco industry. Some catalysts like anhydrous $Cu(SO_4)_2$[1], montmorillonite, Lewis acids[2] and etc are used to synthesize 1,3-dioxolanes from epoxides and ketone/saldehydes. Among these catalysts, anhydrous $Cu(SO_4)_2$ was found to have low yield and long reacting time, montmorillonite shows bad result while applying larger epoxide molecular, some Lewis acids show poor selectivity and yield isomerized products[3].Anhydrous zinc and magnesium halides afforded the rearranged products[4]. By applying $Zn(OTf)_2$ we obtained relatively good result.

Epoxides, ketones/aldehydes and $Zn(OTf)_2$ were added in a sealed reaction kettle under magnetic stiring, at certain reacting temperature and time. Reactants were cooled and analyzed by GC-MS. Conversion and yields are calculated based on GC-MS results. After separation and purification of the product, 1,3-dioxolane, was obtained and analyzed through MS, ^{1}H NMR and IR to assure the structure.

$Zn(OTf)_2$ showed good catalytic performance in the reaction of 1,3-dioxolanes fromation with yields of 76–98% from various epoxides and ketones/aldehydes. So we can see $Zn(OTf)_2$ is an effective catalyst for this reaction. Compared with $Cu(SO_4)_2$, $Cu(OTf)_2$, ZnX_2, and montmorillonite, better results were achieved by $Zn(OTf)_2$ nearly without rearrangement of epoxides to aldehydes or ketones as side products.

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Keywords: *ketones; Synthetic methods; Aldehydes; Cyclization; Lewis acids;*

P-0484

PREPARATION OF A 2, 3-DIALKYL-2--CYANOSUCCINATE COMPOUND AND ITS APPLICATION FOR PROPYLENE POLYMERIZATION

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A 2,3-dialkysuccinate compound, especially 2,3-diisopropylsuccinate compound, is known as an internal donor in a solid catalyst component for olefin polymerization[1]. But the 2,3-dialkysuccinate compound is difficult to be synthesized in industrial scale[1] and diethyl 2,3-diisopropylsuccinate compound was prepared at reaction temperature of -78 °C with only 20% yield.[2] Therefore we design a process for preparing 2,3-di(non-linear–alky)-2-cyanosuccinate compounds, especially 2,3-diisopropyl-2-cynanosuccinate compound, and processes for preparing 2,3-diisopropylsuccinic acid and esters thereof by using the 2,3-diisopropyl-2-cyanosuccinate compound as an intermediate.[3]

A facile synthesis of diethyl 2,3-diisopropyl-2--cyanosuccinate was obtained with 75% yield by treatment of ethyl 2-cyano-3-methylbutyrate with potassium ethoxide followed by condensation the potassium salt of ethyl 2-cyano-3-- methylbutyrate with 2-bromo-3-methylbutyrate at temperature from room temperature to reflux in an aprotic solvent. The structure of obtained diethyl 2,3-diisopropyl-2-cyanosuccinate is confirmed by instrument analyses of IR, ^{1}H NMR, MS(EI) and high resolution mass spectrometry of electro spray ionization (ESI).

The diethyl 2,3-diisopropyl-2-cyanosuccinate is used for the first time as an internal electron donor of a solid catalyst component for propylene polymerization. When a catalyst comprising the catalyst component is used in propylene polymerization, the catalyst exhibits good catalytic activity, and the resulting polymer has a good isotacticity and a broad molecular weight distribution.[4]

In conclusion diethyl 2,3-diisopropyl-2-cyanosuccinate is as good internal electron donor as diethyl 2,3-diisopropylsuccinate for propylene polymerization and is much better in manufacture than diethyl 2,3-diisopropylsuccinate.

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Keywords: *Heterogeneous catalysis; Synthesis design; Polymerization; Synthetic methods; Industrial Chemistry;*

P-0485

POLY(ETHYLENE)-GRAFT-POLY(TERT-BUTYL ACRYLATE) VIA ATOM TRANSFER RADICAL POLYMERIZATION: FUNCTIONAL POLYOLEFINS FROM POLYBROMINATED ALKANES

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Over the last decade, polyolefin-based materials have experienced outstanding growth - not only because of the ease of their manufacture, but also because polyolefin-based thermoplastics can be recycled or combusted with good preservation of energy. Furthermore, since they are solely composed of carbon and hydrogen, the only combustion products are merely carbon dioxide and water[1]. Unfortunately, polyolefins are highly non-polar, which strongly limits their compatibility with other polymers as well as dying and coating applications. Over the last decades, with the development of controlled radical polymerizations techniques, atom transfer radical polymerization (ATRP) has been introduced. ATRP offers access to the synthesis of macromolecules with controlled molecular weights and narrow molecular weight distributions. ATRP is also characterized by a great tolerance for the copolymerization of various functional monomers. Meanwhile, brush- as well as graft-copolymers have been prepared *via* 'grafting to' and 'grafting from methods, the 'grafting from' method certainly being the best approach in terms of brush density.

What all ATRP-based methods have in common is the use of *activated* alkyl halides, e.g., of a-bromocarboxylic esters. Such *activated* halogen-alkyl bonds are weaker than standard alkyl halide bonds and thus more susceptible to homolytic cleavage by the Cu (I) complex. Vice versa, to the best of our knowledge, there are no reports on the ATRP involving *non-activated* alkyl halides. Starting from poly-halogenated polyethylene, such an approach would offer a highly useful access to functionalized polyolefins. Starting from Poly-brominated linear PE, we successfully developed an ATRP-based synthesis of a series of novel well-defined functional poly(ethylene) graft copolymers with different graft densities and graft lengths thereby developing a straight-forward access to functional polyolefins[2].

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Keywords: *Poly(ethylene); Atom transfer radical polymerization; comb-copolymer;*

P-0486

STUDY OF ANTIFUNGAL AND ANTIBIOTIC DRUGS LOADED MICROSPHERES BASED ON POLY(DL-LACTIDE) AND POLY(DL-LACTIDE-CO-CAPROLACTONE)

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In an effort to develop a new way of Drug Delivery Systems, two biodegradable polymers, poly(DL-lactide) (PLA) and poly(DL-lactide-co-caprolactone) (PLC) were used for the formulation of microspheres loaded with antifungal drugs (Nystatin and Amphotericin B) and antibiotics (Tetracycline and Doxycycline) respectively.

Microspheres were prepared using the solvent evaporation technique by changing the masses of drugs introduced. They were then evaluated for percentage yield, drug entrapment, particle size, morphology, drug-polymer interaction, stability and *in vitro* drugrelease.

The particle size analyzer showed a homogeneous size distribution for the microspheres, ranging between 80 to 110 µm. The maximum drug entrapment reached 20% and 81% for PLC microspheres loaded with Nystatin and Amphotericin B respectively. As for Tetracycline and Doxycycline, the drug entrapment was 30% and 18% respectively. Scanning Electron Microscopy (SEM) and Optical Microscopy revealed that the microspheres have a spherical shape with a porous surface. Fourier Transform-Infrared (FT-IR) study confirmed the absence of chemical interaction between the drug and the polymer. Stability study indicated no appreciable difference concerning the degradation of the microspheres after 3 months of storage at different temperatures. The *in vitro*release study was carried out for the formulations with the highest percentage of encapsulation. For Nystatin and Amphotericin B, the drug release needed few days in comparison with Tetracycline and Doxycycline, which required only several hours to go to completion.

P-0487

THE SYNTHESIS AND CHARACTERIZATION OF POLYALPHAOLEFIN BY USING ALUMINUM BASED LEWIS ACID CATALYST

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Polyalphaolefin (PAO) is the synthesis lubricant that superior to petroleum-based and mineral-based lubricant in the terms of physical, chemical characteristics such as low pour point, high viscosity index (VI), thermal stability. We have synthesized a several kinds of PAOs using 1-pentene, 1-hexene, 1-octene, 1-dodecene as monomer and different types of aluminum based lewis acids as cationic polymerization catalyst. The control of polymerization performance (yield, activity) and physical properties of PAO (molecular weight, kinetic viscosity, pour point, viscosity index) could be achieved by changing polymerization parameters such as polymerization time and temperature, the type and concentration of monomer and catalysts. In view of polymerization yield and molecular weight of PAO, $Et_3Al_2Cl_3$/t-butylchloride catalyst system was superior to another used aluminum based catalysts. Microstructure of PAO was investigated by means of TOF-MS (Time of Flight-Mass Spectroscopy) studies. The important parameters for lubricant such as VI and pour point were strongly depended on microstructure of PAO i.e. branch length. In other words, the VI value of PAO increased with increasing the branch length of PAO.

Keywords: *Polyalphaolefin; Aluminum; Catalyst; Polymerization; Lubricant;*

P-0488

THE STUDY OF INFLUENCE OF MICRO ADDITIVES OF SINGLE-WALL CARBON NANOTUBES ON STRESS-STRAIN PROPERTIES AND STRUCTURE OF NOVEL POLYURETHANE BLOCK COPOLYMERS

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Carbon nanotubes are capable to change properties of polymers, such as mechanical strength, the Young modulus, the tensile strain, optical properties etc. However, the insufficient attention is given to studying of influence of micro additives of single-wall carbon nanotubes (SWCNT) on the polymers structure.

Polyurethane block copolymers (PUBCP) were synthesized for the first time in the present work by interaction of oligodiethylenglycol adipate (ODGA, crystallization temperature $T_c = 60$ °T), of the mixture of symmetric with asymmetric diisocyanates and of agents of chains extension in solution at room temperature. The influence of micro additives of SWCNT on stress-strain properties and structure of PUBCP was studied.

PUBCP possess quite high Young modulus (about 450 MPa) up to T_c. It undergo orientation deformations up to 900 % with forming of the strong rigid films (rupture strength ~ 45 MPa) at stretching after achievement of the limit of forced rubberlike elasticity. The oriented samples completely restore their initial sizes at the heating above T_c.

Introduction of SWCNT in PUBCP (0.002 – 0.008 wt. %) leads to various changes of stress-strain properties and structural parameters. Changes of supramolecular structure of polymer under the influence of SUNT consist in increase in the Young modulus and tensile strain for 20-30 %. At the same time, tensile strength of the filled and unfilled samples does not change practically. The SWCNT additives influence noticeably on relaxation behavior of polymer. Thus, recovery of the initial sizes of the samples, containing up to 0.008 wt. % of SWCNT, after deformation requires more high temperatures and prolonged time in comparison with unfilled samples.

Data of DSC and analysis of X-ray diffraction patterns of PUBCP, containing SCNT, testify considerable structural changes in comparison with unfilled polymer. The reasons of influence of SCNT on structure and, therefore, properties of synthesized PUBCP are discussed.

Keywords: *single-wall carbon nanotubes; stress-strain properties and structural parameters; Polyurethane block copolymers;*

P-0489

SYNTHESIS OF NONAPEPTIDE (B22-B30) OF INSULIN B-CHAIN USING MODIFIED SOLID PHASE METHODS WITH AND WITHOUT MICROWAVE TECHNIQUE

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The biological activity of Insulin is known to be closely related to the C-terminal nonapeptide (B_{22}-B_{30}) fragment of its B-chain. This does not necessarily mean, however, that each of the amino acid residues of the nonapeptide fragment is essential for its activity.

Keywords: *Insulin; Peptide; Amino Acids; Modified Solid Phase and Microwave.;*

P-0490

ELECTROCHEMICAL CHARACTERIZATION OF PVDF BASED POLYMER ELECTROLYTES FOR SECONDARY BATTERIES

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PVDF-based polymer electrolytes have many different uses according to the intended use. For example; also being used as electrolyte in rechargeable batteries[1], they can also be used in fuel batteries (electrolyte),[2] besides, they can be used as a binder for the preparation of cathode material in rechargeable batteries,[4] as an electrolyte for supercapacitor applications[5] and as polymer electrolytes in solar batteries.[6]

The chemical and the thermal stability that the PVDF-based gel polymers show, make such type of materials attractive for battery and fuel cell applications. Being among the cheapest fluoropolymers and having a wide melting point range (115 °C–175 °C), PVDF is a processable polymer which also has properties such as low surface tension [referans]

In this study; the electrochemical stability window of the membrane has been evaluated with the recyclable voltametry technique using the 3 (triple) electrode system. All electrochemical measurements have been performed within glove box (argon gas cabin). Ac conductivity values of the membranes containing with Li salts have been found within the range of 10^{-5}–10^{-6} S/cm. In this study lithium salts such as $LiClO_4$, $LiPF_6$ and $LiBF_4$ were used by dissolving them in solvents like PC(propylene carbonate), EC (ethylene carbonate), DEC(diethylene carbonate). The obtained polymer electrolyte membrane has been characterized in Li (anode)?Polymer electrolyte?LiCoO2(cathode) battery assembly.

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Keywords: *rechargeable battery; ionic conductivity; gel polymer electrolyte;*

P-0491

ELECTROCHEMICAL CHARACTERIZATION OF PVDF BASED POLYMER ELECTROLYTES FOR SECONDARY BATTERIES

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References:

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5. YW Chen-Yang *; YT Chen; CC Lia; HC Yu; YC Chuang; CH Su, YT Lin, Preparation of UV-filter Encapsulated Mesoporous Silica with High Sunscreen Ability, Mater. Lett., Vol.65, No.6 p.1060–1062, 2011

Keywords: *secondary batteries; gel polymer electrolyte; ionic conductivity;*

P-0492

SYNTHESIS OF THE SIDE CHAIN DEUTERATED BRASSINOSTEROIDS

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Since the discovery of brassinolide in 1979, about 70 related compounds called as brassinosteroids (BS) have been identified in plants. Because of a very low content of BS in natural sources, only few of them have been isolated as individual compounds. In most cases, their presence in plant sources has been proven by instrumental methods. The necessary prerequisite for such investigation is elaboration of appropriate biochemical hypothesis and the presence of a set of compounds which are expected to be found. These compounds have to meet some requirements. At least three deuterium atoms should be present in the molecule to avoid possible interferences with the peaks [M+1] and [M+2] belonging to natural ^{13}C and ^{18}O containing species.

The identification procedure implies feeding of plants with labeled precursors followed by analysis of plant extracts by instrumental methods (GC/MS or LC/MS). The success of search is very much influenced by the proper choice of labeled compounds. The label should be located in a metabolically inert position and not be subjected to spontaneous isotopic exchange.

In the present work, new results concerning the preparation of BS and their biosynthetic precursors with three deuterium atoms in the side chain will de discussed.

Keywords: *Brassinosteroids; Labeling; Brassinolide; Epibrassinolide;*

P-0493

TRILOBOLIDE PHARMACOPHORE MODIFICATIONS

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Trilobolide is a sesquiterpene lactone isolated from *Laser trilobum*. This compound was previously found to play a role as inhibitor of sarco/endoplasmic reticulum Ca^{2+}-ATPase activity (SERCA)[1]. Moreover, the farmacophores of this unique compound are known and this contribution is coming with view on "vicinal diol" farmacophore at positions 7 and 11 of the guaianolide skeleton. It was previously demonstrated, that the similar diol of the structurally related compound thapsigargin can be easily transformed to epoxide[2]. Trilobolide was transformed to 7,11-epoxide which was used as the starting material for further syntheses. The modifications of epoxide may well be done by nucleophilic opening of epoxide giving corresponding hydrines. In this work, the primary results from epoxide opening reactions are described. It is expected that such synthetic modifications may change the biological behaviour of such trilobolide hybrids.

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Keywords: *Terpenoids; Biological activity; Synthetic design;*

P-0494

DETERMINATION OF CADMIUM BY ADSORPTIVE STRIPPING VOLTAMMETRY USING PYROCATECHOL VIOLET CHELATING AGENT

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The adsorptive collection of Cd (II) complex with pyrocatechol violet ligand, coupled with the square wave voltammetric technique, yields a very sensitive electroanalytical procedure for the determination of cadmium in various industrial samples. The optimized experimental conditions include: supporting electrolyte (carbonate buffer), pH (9.5), pyrocatechol violet concentration ($1.5?10^{-5}$ moll^{-1}), accumulation time (30 s), accumulation potential (0.0 V), scan rate (200 mV s^{-1}), pulse amplitude (0.05 V) and SW frequency (50 Hz). The monitored stripping voltammetric current was linear over the range of $7.5?10^{-8}$–$1.75?10^{-7}$ moll^{-1} and the detection limit was 0.66 ppb. The relative standard deviation was calculated as 1.02% (n = 10) for $1?10^{-7}$ mol l^{-1} Cd(II) and the obtained electrochemical signal was stabile for up to 120 minutes. Possible interferences by either co-existing metal ions or other chelating agents were also investigated. The applicability of the developed method for the determination of Cd element was assessed by the analysis of various industrial and environmental samples. The accuracy of the obtained voltammetric analytical results was validated by comparing with that obtained by atomic absorption spectrometry and conducting the necessary statistical evaluation.

Keywords: *Electrochemistry; Voltammetry; Cadmium;*

P-0495

DETERMINATION OF PKA VALUE OF IRINOTECAN USED FOR TREATMENT OF COLORECTAL CANCER BY REVERSED PHASE LIQUID CHROMATOGRAPHY

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Colorectal cancer, also called coloncancer or large bowel cancerincludes cancerous growths in the colon, rectum and appendix. It is the thirdmost common form of cancer and the second leading cause of cancer-related deathin the Western world [1]. Colorectal cancer is the third mostcommon form of cancer appears in our country and it can also occur in everyage, but above the 90% of the patients are more than 40 years old [2]. Recently, combined active drugs in the treatment of colorectal cancer was usedbecause of more efficiently destroy the tumor cells in the standard therapy forpatients. Irinotecanwhich is one of the drugs for this purpose, an antineoplastic drug usedintravenously in the treatment of advanced colorectal cancer. It is isolatedfrom Camptotheca acuminata which issitotiksik a tree that grows in China [3].

The ionization constant is an importantphysico-chemical parameter of a drug and the knowledge of this parameter is offundamental importance in a wide range of applications and research areas. Inthis study pK_a values of irinotecan were determined and the effectof the mobile phase composition on the ionization constant was studied bymeasuring the pK_a at different acetonitrile-water mixtures, 35,40,45, 50 % (v/v) using LC-UV method.

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P-0496

SUPRAMOLECULAR COMPLEXES FORMATION. POSSIBILITIES OF MASS SPECTROMETRIC STUDIES

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In supramolecular complexes the molecules or ions are held together by non-covalent interactions: Host + Guest <=> {Host, Guest}. Usually, compounds like cyclic ethers, cyclodextrines, or other macrocycles might act as hosts while various organic/inorganic cations, anions, neutral molecules etc. are playing the role of guests.

The paper deals with the application of mass spectrometry (MS) for fast screening of variour host-guests combinations in order to find out the formation of supramolecular complexes and/or to search for new potential drug carriers or to decrease their toxicity.

MS was done using either matrices, laser desorption ionization (LDI) or surface assisted LDI. Mass spectrometric analysis was used because the reactions can also be done directly on the MS target and several combinations can be examined with the minimum amount of often scarce and expensive reagents.

Several examples of supramolecular complex formation using different types of macrocycles (cyclodextrins, cucurbit[n]urils, etc.) as hosts, and either drugs like antivirals, cancerostatics or inorganics including nanoparticles as guests, will be given and discussed.

The proposed application of mass spectrometry represents fast, efficient and economic way to search for the formation of new supramolecular complexes. The results might find application in medicine.

Keywords: *Mass Spectrometry; Supramolecular complexes;*

P-0497

ELECTROCHEMICAL OXIDATION OF AQUEOUS PROPYLENE GLYCOL WASTE

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Advanced oxidation processes are currently used to treat industrial effluents. However, they have some major drawbacks if wastewater contents the large amount of inorganic chlorides. In this context, oxidative electrochemical technologies offer an alternative solution to purification of wastewater formed under oxide propylene production. The electrochemical oxidation of this wastewater contents propylene glycol and the chloride ions in strong basic media has been studied.

Chemical oxygen demand (COD) and concentration of the chloride ions were determined using a chemical analysis. The concentrations of propylene glycol and products of their electrochemical oxidation were determined by optical spectroscopy, IR-spectroscopy, and chemical analysis. The optical absorption spectra were registered on Shimadzu UV-2450 spectrophotometer. The diffuse reflectance IR-spectra were registered by the FTIR spectrometer "System-2000" by Perkin Elmer. The oxidation of propylene glycol was carried out in a single compartment electrochemical cell. Stainless steel electrodes were used. The composition of the wastewater used in the experiments was, 32800±500 mg/dm^3 (Cl^-), 1500-2500 mg/dm^3 (COD), and pH 11-12. The current density used was 75 mA cm^{-2}. Voltage used was 4.3 V.

The main by-products of propylene glycol decay under electrochemical oxidation are established. Maximum of the organic waste mineralization is ~80%. Time of the treatment increases from 10 to 30 min with increasing COD from 1500 to 2500 mg/dm^3 for this degree of mineralization. The concentration of the chloride ions remains unchanged.

Keywords: *Electrochemical oxidation; Propylene glycol; Wastewater;*

P-0498

FLUORESCENCE DETECTION OF NUCLEOTIDES UNDER PHYSIOLOGICAL CONDITIONS USING COPPER(II)-COMPLEXES

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Detecting anionic species of biological importance like phosphates with the help of chemosensors has attracted considerable attention in recent years.[1] Especially high selective receptors for adenine containing nucleotides are of particular interest.[2]

Herein we present a novel approach for fluorescent sensing of nucleotides based on designing the ligands that not only contain fluorescent dyes but also a recognition site for metal ions like copper(II) which are known for strong interactions with phosphates. Together with analytes these ligands can form ternary copper(II)-complexes in aqueous solution.

The ligand works as key component that determines the selectivity and generate an analytical signal. We synthesized ligands **1-4** which in the presence of copper(II)-salts showed moderate selectivity for ATP and GTP according to fluorescence measurements. The recognition mechanism for each ligand was investigated. It was shown that selectivity can be achieved using a combination of several ligands with copper(II)-salts.

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Keywords: *Fluorescence; copper; nucleotides; sensor;*

P-0499

OPTIMIZATION OF SODIUM BICARBONATE PRODUCTION FROM BORAX BY TAGUCHI METHOD

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The demand for boron products of industrial companies in the world are increasing every passing day. Turkey has about 72 % of the known boron reserves of the world. An important part of Turkey's boron reserves is occurred colemanite, tincal and ulexite minerals. It is of great importance that variety of boron compounds produced from boron minerals have increased and that compounds have produced in minimum cost. Tincal is dissolved in hot water and is separated from impurities by filtration and is obtained as borax decahydrate (borax). Although there are many studies concerned with the production of different boron chemicals from borax, the studies with regard to sodium bicarbonate from borax are scarcely available.

In this study, the sodium bicarbonate production from borax decahydrate in ammonia solutions saturated by carbon dioxide gas in pressure reactor was studied and the effects of relevant parameters, namely; reaction temperature, solid-to-liquid ratio, reaction time, pressure and ammonia concentration have been investigated on the sodium bicarbonate production from borax by using the Taguchi method. The chosen experimental parameters were as follows: reaction temperature, 45–60 °C; solid-to-liquid ratio, 0.69-0.92 g/mL; reaction time, 30- 60 min; pressure, 5-20 bar; ammonia concentration, 2,82-5,65 M. Steering speed was stable at 500 rpm. The optimum conditions have been determined between the sodium bicarbonate production efficiency from borax and relevant parameters by means of variance analysis by using the statistical computer software. The optimum conditions were found to be as follows: reaction temperature, 60°C; solid-to-liquid ratio, 0.77 g/mL; reaction time, 50 min; pressure 20 bar; ammonia concentration 3.7634 M. In these conditions, produced sodium bicarbonate has approximately to 70% efficiency and 98% purity.

Keywords: *Boron; High-pressure chemistry; Industrial chemistry; Solid-phase synthesis; Carbon dioxide;*

P-0500

INVESTIGATION OF SODIUM BICARBONATE PRODUCTION FROM BORAX IN AMMONIA SOLUTIONS SATURATED WITH CARBON DIOXIDE GAS UNDER PRESSURE

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The most important mine that Turkey has got approximately 72% of the world reserves is the boron minerals. Boron products such as borax decahydrate, borax pentahydrate, boron nitride, zinc borate, boric acid, sodium pentahydrate, boron oxide, disodium octaborate tetrahydrate, anhydrous borax are produced from boron minerals. In this study, sodium bicarbonate which is an important industrial input is aimed to be produced by using borax decahydrate and CO_2 as raw materials for both the highest yield and purity. In addition, it is expected to be contributed positively to the reduction of CO_2 causing global warming.

In this study, the optimum conditions of sodium bicarbonate production from sodium tetraborate decahydrate ($Na_2B_4O_7.10H_2O$) in ammonia solutions saturated with carbon dioxide gas under pressure is investigated. Experiments were carried out by using the experimentation method with change of one factor at a time (OFAT). The chosen experimental parameters were as follows: reaction temperature (45-65°C), solid-liquid ratio (0.69-0.92 g/mL), reaction time (30-60 min), pressure (5-30 bar), ammonia concentration (2,82-5,65 M) and crystallization temperature (0-50°C). As the target of optimization was both the highest yield and purity, solid amount(g) / B_2O_3% was chosen as the optimization criterion. The value of optimization criterion (solid amount(g)/%B_2O_3) had increased, $NaHCO_3$ purity and yield increased, indicating B_2O_3% decreases and solid amount increases. As a result, the criterion of optimization observed to increase up to a certain point with increasing reaction temperature, solid-liquid ratio, reaction time, pressure, ammonia concentration and crystalization temperature. The optimum conditions were found to be as reaction temperature, 60°C; solid-to-liquid ratio, 0.77 g/mL; reaction time, 50 min; pressure, 20 bar; ammonia concentration, 4.7043 M. In these conditions, produced sodium bicarbonate has solid amount(g) / %B_2O_3 = 10.04 and 97.75% purity.

Keywords: *Borates; High-pressure chemistry; Solid-phase synthesis; Carbon dioxide; Industrial chemistry;*

P-0501

DYE-SURFACTANT INTERACTION STUDIED BY PHOTODYNAMIC PARAMETERS

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Pyronine Y (PyY) which is a positively charged dye compound is a xanthene derivative dye compound used in this study. Xanthene derivatives are very efficient laser dyes and fluorescent probes that offer outstanding photophysical and photodynamic properties. Therefore, PyY is used in model biologic systems and laser spectroscopy widely. Photophysical and photodynamic properties of this kind of dyes depend on the media. Thus, it is important to determine behavior of PyY in different media.

In this study, the photodynamic of PyY compound in the negatively charged sodium dodecyl sulfate (SDS) surfactant medium has been examined. Pyronin Y concentration was kept constant and experiments were carried out as a function of temperature in SDS surfactant solutions prepared at different concentrations. Photodynamic parameters were fluorescence anisotropy, rotational diffusion times and microviscosity of the probe environment. Experimental temperature range was 10 to 60°C and the effect of temperature on surfactant-dye interactions has been observed via photodynamic parameters.

Fluorescence anisotropy is a reflection of rotational diffusion and used in molecular biology studies such as protein-ligand interactions, protein denaturation, and membrane activity.

As a result, steady-state fluorescence anisotropy values obtained with surfactants below the critical micelle concentration were low. This observation is due to the probe environment that permits probe molecules move freely without any restriction. The decrease of anisotropy values at higher temperatures is also an indication of the deformation of the micelle structure with temperature increase. It has been observed that the steady-state fluorescence anisotropy values calculated for PyY at 10^{o}C in 20 mM SDS surfactant solution was equal to the limiting anisotropy value of 0.373±0.002 for xanthene family dye compounds. Moreover, the largest value of microviscosity value was determined at the critical micelle concentration of SDS. It stated that the micro environment of PyY is more rigid in this condition.

Keywords: *Dye-surfactant interaction; Pyronine Y; Photodynamic;*

P-0502

INVESTIGATION OF MOLECULAR INTERACTIONS BETWEEN COUMARIN 35 AND BOVINE SERUM ALBUMIN: FLUORESCENCE RESONANCE ENERGY TRANSFER (FRET)

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Coumarin 35 (C35) is also named 7-dietil amino-4-trifloro methyl coumarin or coumarin 481. It is dye compound derived from 7-amino coumarins. 7-amino coumarins are the important groups used as analgesics, anticoagulants, fluorescence probes and sensitizer in photo processes.[1] Serum albumin is the abundant protein in plasma and plays a major role to the distribution of various biologically active compounds such as metabolites, drugs and other organic compounds.[2] Bovine serum albumin (BSA) was selected as a model protein to study interactions with C35.

In this study, the molecular interaction mechanism between C35 and BSA were studied by using fluorescence spectroscopy techniques. The fluorescence properties of dye in the free state and interacted with BSA were investigated. The distance r between BSA (donor) and C35 (acceptor) was calculated using by Förster's theory in different temperatures. Förster's theory known as Fluorescence Resonance Energy Transfer Method (FRET) is often used for measuring molecular distances in various systems as biological, macromolecular systems.[3] Accordingly, the efficiency of energy transfer between the donor (BSA) and the acceptor (C35), molecular distances; R_0 (Förster radius) and r (the binding distance) in between C35 and BSA were determined in different temperatures. Synchronous fluorescence spectra supplied information about the conformational changes in BSA. Synchronous fluorescence spectra indicated that the interaction of BSA with C35 was affected from the conformation of tyrosine residues micro-environment. It was revealed that C35 is more accessible to the tyrosine residues than to tryptophan residues.

Keywords: *Bovine Serum Albümin (BSA); Coumarin 35 (C35); Fluorescence Resonance Energy Transfer Method (FRET); Fluorescence spectroscopy;*

P-0503

BINDING PROPERTIES OF BOVINE SERUM ALBUMIN TO THE COUMARIN 35: SCATCHARD PLOT AND DOUBLE LOGARITHMIC PLOT.

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The interaction between coumarin 35 (C35) and bovine serum albumin (BSA) were studied by using UV-Vis. absorption and fluorescence spectroscopy techniques. In our different study, the binding distance, the conformational changes and the energy transfer between BSA and C35 were determined. In this paper, the binding equilibrium between BSA and C35 was studied by using two different methods. There are many methods for the determination of binding constants. Because determination of binding constants is useful tool for both to understand and characterize the protein – ligand interactions,[1] The most common methods, scatchard and double logarithmic plots, were exploited for investigation. In this study, the binding constants from scatchard and double logarithmic plots for the C35-BSA systems were calculated for different temperatures. It was determined that there is a decrease in binding constant values with increasing temperature for both methods. The high linearity was obtained for the plots. It was concluded that the presence of a single class of binding sites is valid.[2]

Keywords: *Bovine Serum Albümin (BSA); Coumarin 35 (C35); Fluorescence spectroscopy; Scatchard Plot; Double Logarithmic Plot;*

P-0504

A TWO DIMENSIONAL SEPARATION FOR THE ENANTIOSELECTIVE DETERMINATION OF HEXABROMOCYCLODODECANE (HBCD) FROM ENVIRONMENTAL SAMPLES

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A new method has been developed to determine the enantiomers of the α-,β- and γ-isomers of the brominated flame retardant Hexabromocyclododecane (HBCD) undisturbed from each other. While often (+) α HBCD tends to coelute with (+) β- and (+) γ-HBCD in the enantio-selective HBCD analysis, we use a two dimensional high performance liquid chromatography (HPLC) approach to separate the non labelled isomers and their 13C-labelled analogues on a conventional column and transfer the isomers separately by heart cuts to an enantio-selective column. The enantio-selective column thus acts as a real second dimension. For this approach the first separation is set to stop flow after the first isomer is transferred to the secondary enantio-selective column. Only when the secondary column is reconditioned the primary chromatogram is developed further and the other two isomers are transferred to the enantio-selective column. 13C-labelled isomers are separated in the same way and allow enantio-specific quantification by isotope dilution. Detection is performed by tandem mass spectrometry utilizing electrospray in negative mode.

The result is a completely undisturbed enantio-selective separation for α-HBCD, the predominating isomer in high trophic level biota. Different data treatment methods (using area values, area values referred to the corresponding internal standard area and full internal standard calibration) are discussed. The performance of the system has been tested by repeated analysis of fish oil and a multitude of environmental samples.

P-0505

THE INTERACTION IN SULPHANILAMIDES – AZO DYES SYSTEMS AND THEIR ANALYTICAL APPLICATION

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Spectrophotometry is used for sulphanilamides (SA) quantity control in antibacterial preparations. However, it is not suitable for complex medicines analysis because of insufficient selectivity of known spectrophotometric reagents.

It was established that diazotized sulphanilamides interact with acid monoazo dye Tropaeolin O (Tr O), heterocyclic azoreagents 4-(2-pyridylazo)resorcinol (PAR) and 4-(2-thiazolylazo)-resorcinol (TAR) and o,o'-dihydroxo substituted azo dyes eriochrome black T, eriochrome blue-black R and eriochrome blue SE forming coloured compounds. Optimum conditions for SA interaction with azo reagents were studied: pH at the presence of proper buffer solution (neutral or basic media depending on the reagent) and corresponding reagents excess (1.5-6-fold). Effective molar absorptivities for SA-azo reagents systems approximately are 10^3-10^4 M^{-1} cm^{-1}. Developed methods are suitable for SA microgram amounts determination in complex mixtures.

Diazotized sulphanilamides azocouple with Tr O, PAR and TAR forming disazo dyes, which is confirmed by new absorbance maximum appearance at 590-615 nm for product solutions. This assumption is confirmed by voltammetric studies. We observed two peaks of azo-groups reduction on products polarogramms. Potentiometric titration and spectrophotometric study in atmospheric oxygen presence and in oxygen free media verified that in SA–azo reagents systems redox interaction did not take place.

Decrease of azo dyes absorbance maxima and appearance of other maximum are observed on UV-Vis absorbance spectra of products of diazotized SA interaction with o,o'-dihydroxo substituted azo dyes. Voltammetric studies also showed that due to SA diazonium salt azo-groups reduction peak is decreased and a new shoulder appears for all products. Potentiometric redox titration confirmed the redox nature of interaction in diazotized SA-o,o'-dihydroxo substituted azo dyes systems (azo dyes are oxidized), because significant changes of systems redox potentials were observed on titration curves. UV-Vis spectra of obtained compounds showed that O_2 does not react with azo dye.

Keywords: *Azo compounds; Analytical Methods; Oxidation; Sulfonamides; UV/Vis spectroscopy;*

P-0506

MOLECULAR BEHAVIOR OF COUMARIN 120 IN REVERSE MICELLE CONTAINING POLYMER

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7-amino-coumarin derivatives are used as solvation probes in various micro-environments. When amino-coumarin dyes were excited with electromagnetic radiation, intramolecular charge transfer (ICT) takes place from the electron donating amino group to the electron withdrawing carbonyl group of the coumarin ring. This process causes a large change in the excited state dipole moment. Due to difference in dipole moments, ICT occurs gradually with increasing solvent polarity. In addition, depending on the solvent-solute interactions, energy gap between the ground and the lowest excited singlet state reduced. This causes a Stokes' shift of fluorescence emission.

Reverse micelles consist of surfactant molecules dispersed in a non-polar organic solvent and polar solvent (usually water), forming water pool. The size of water pool is determined by W_0 (water/surfactant molar ratio). $W_0<15$ systems are called reverse micelles, whereas $W_0 \geq 15$ systems are known as microemulsion. The interactions between water-soluble polymers and reverse micelles have gained an importance in recent years. Polyvinylpyrrolidone (PVP) is one of these kinds of polymers. It is used applications such as pharmaceuticals, cosmetics, medicine, textiles, paper and detergents.

In this study, the concentration of 1 mg/ml PVP stock solution was prepared. Reverse micelle systems containing distilled water were added to the solution of PVP instead of water. Absorption and fluorescence (λ_{exc}=300 nm) measurements of Coumarin 120 were taken.

Fluorescence emission spectra of C120 were indicated red shifts with increasing values of W_0. Red shift at fluorescence spectrum is observed because polarity of water pool in reverse micelles increases with increasing the value of W_0. However, fluorescence intensity of C120 increases at low values of W_0 in reverse micelle systems prepared with PVP polymer. It was shown that the polarity of water pool with the presence of PVP is lower than in the absence of PVP.

Keywords: *Coumarin 120; Intramolecular Charge Transfer (ICT); Fluorescence; Reverse Micelle; Polyvinylpyyrolidone (PVP);*

P-0507

THE STUDY OF STATIONARY PHASES SPECIFICITY BY LINEAR SOLVATION ENERGY RELATIONSHIPS

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The analysts working with high performance liquid chromatography (HPLC) look for a better understanding of retention mechanism. This trend is connected with designing and synthesis of new stationary phases for HPLC. The solvation parameter model by Abraham is the most popular method for the determination of interactions taking place during the chromatographic process. It is based on the linear solvation energy relationships (LSERs) and allows obtain information about the stationary phase retention properties. Therefore its application is especially interesting for the study of new types of stationary phases.

The solvation parameter model may be described by equation:

$$\log SP = c + rR_2 + sp_2^H + aa_2^H + bb_2^H + vV_x$$

where: log SP is the property of a series of analytes, *R* is an excess molar refraction, π_2^H the solute dipolarity/polarizability, α_2^H, β_2^H the overall or effective hydrogen-bond acidity and basicity, V_x – the McGowan characteristic volume. These are five interactions causing differences in retention mechanism and cause suitable selectivity and resolution.

The main goal of the study was the investigation of retention of 50 analytes with the use of LSER model on seven different HPLC packing materials. Furthermore six of them have been specially synthesized and are functionalized with octadecyl chains (of two different carbon load), alkylamide, cholesterol, alkyl-phosphate, phenyl groups. Commercially available immobilized artificial membrane has been also used. Acetonitrile and methanol were used as mobile phase components to compare the influence of both organic solvents on interactions occurring between solute, stationary and mobile phase.

Stationary phases used in the investigations are structurally very different. However it has to be pointed out that for several of them significant differences in interactions were not observed. It concern octadecyl, alkylamide, cholesterol, phenyl phases. The *v*coefficient is always the largest and of positive sign, thus exerting the greatest influence on retention. Characteristic to these phases is that the acidicity is insignificant in contrast to basicity, which is the main hydrophilic term. Different situation occurs for alkyl-phosphate (SG-P-C10) and immobilized artificial membrane (IAM) packings. Both phases have relatively low *v* and high *b*. Moreover retention of solute on IAM phase is influenced also by hydrogen bond acidity. Contrary for SG-P-C10 also high dipolarity of solute increase its partitioning to stationary phase.

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Keywords: *stationary phases; linear solvation; energy relationships;*

P-0508

IDENTIFICATION AND DETERMINATION OF GENTAMYCIN AND ITS METABOLITES FROM HUMAN PLASMA AND CELL CULTURE MEDIA BY SPME-LC/MS^N

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Determination of biologically active compounds from various matrices, including environmental and biological samples is a serious problem in a modern analytical chemistry. The most relevant matrices to be analyzed for this purpose are plasma or blood, due to providing a good correlation between their concentration and pharmacological effects. One of the major tool is the combination of high-performance liquid chromatography and mass spectrometry (LC/MS^n). The main aim of this investigation was to apply a fast and sensitive extraction technique using electrochemically prepared a new polymeric coatings as sorbents for solid phase microextraction (SPME). Polypyrrole (PPy), polythiophene (PTh) and poly(3-alikilothiopenes) SPME coatings were used and evaluated their ability to extract gentamycin from human plasma samples and cell culture media as well. Mass spectrometric parameters were optimized for target compound in positive ion mode over the *m/z* 100–500 range. Quantitation was done using multiple reaction monitoring (MRM) mode to monitor precursor ion at $[M+H]^+$ to product ion transition of 478 ? 322 for gentamycin (GEN). Validation data for accuracy and precision for intra- and inter-day were good and satisfied FDA's guidance: CV between 0.39% and 9.83% and accuracy between 95.7% and 111.3% for all compounds. Developed method can be used for the quantitative analysis of selected biologically active compound, and provide a potential application to study the metabolism and pharmacokinetics of other drugs from different medical classes from the biological matrices. In conclusion, although various LC-MS/MS methods have been developed and reported in the literature for the measurement of gentamicin, the described method by us appears to be particularly promising. It is rapid and accurate, and can be applied as a routinely used in clinical laboratories.

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Keywords: *gentamycin; human plasma; cell culture media; SPME-LC/MSn;*

P-0509

OPTICAL PROPERTIES OF MNO$_2$ THIN FILMS IN NON-AQUEOUS ELECTROLYTES

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In recent years, supercapacitors (SCs) have attracted much attention for their power enhancement compared to batteries and fuel cells, and higher energy densities than common capacitors [1]. Among several transition metal oxides (RuO_2, IrO_2, NiO, CoO_x, SnO_2 and MnO_2) tested as electrode materials for pseudocapacitors [1, 2, 3, 4], MnO_2 due to its low cost, satisfactory electrochemical performance and natural abundance is considered as one of the most promising materials for SCs in many technological applications ranging from mobile devices to electric vehicles [2, 5].

In this contribution, we will report on the electrochemical behaviour of MnO_2 in protic ionic liquid (PIL) electrolytes obtained by a mixture of a base like 2-methoxy-pyridine (2-MeOPy) and an acid (trifluoroacetic) that were shown to sustain pseudocapacitance in this oxide. Thus, the MnO_2 films electrochemically deposited onto ITO substrates were studied and characterized. Further information about synthesis, characterization by SEM, XRD, CV and UV-vis spectroscopy and stability performance will be reported. Spectroelectrochemical experiments have been carried out to study the changes in the optical properties of the MnO_2 films which are linked to the oxidation state of the material. Further developments on task-specific ionic liquids for electrolytes in metal-oxide based supercapacitors are expected to increase their charge storage properties.

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Keywords: *Ionic liquids; UV/Vis spectroscopy; Manganese;*

P-0510

CHANGES IN LIPID PROFILES OF PATIENTS WITH CARDIVASCULAR DISEASES

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Cardiovascular diseases (CVDs) are one of the most common cause of death in the world. It is strongly connected with the change of the lipidome. Differences between samples of healthy volunteers and patients are studied in our project. The group of 50 men contained 5 subgroups (healthy volunteers, obese and 3 types of CVDs). Each sample was divided into erythrocytes, plasma and 3 lipoproteins fraction (VLDL, LDL, HDL). Samples were extracted using Folch method[1]. The total lipid extract was separated using HILIC-LC/ESI-MS into individual polar classes of lipids[2]. Non-polar lipid extracts were prepared using hexane/methanol/water and analyzed by NP-HPLC/APCI-MS. Fatty acid methylesters (FAMEs) were prepared using the transesterification with sodium methoxide and quantified by GC/FID. There are differences in profiles of lipids and FAMEs between each type of samples. Changed levels of polar class lipids between healthy control and patients were observed in our chromatograms. An increase of relative percents of some FAMEs for patients was observed in GC/FID chromatograms. These changes have will be important for CVDs biomarker discovery in our future studies.

Acknowledgement: *This work was supported by the grant project No. 206/11/0022 (Czech Science Foundation).*

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Keywords: *lipid; cardiovascular diseases; mass spectrometry;*

P-0511

DETERMINATION OF SULFAMETHIZOLE USING CARBON PASTE ELECTRODE

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Two new methods were developed for the electrochemical determination of sulfamethizole, sulfonamide antibiotic used for the treatment of urinary tract, using carbon paste electrode. The first method employs differential pulse voltammetry (DPV) and is aimed to the determination of sulfamethizole in samples of pharmaceutical formulations; the other method uses HPLC with amperometric detection and is aimed to the determination in biological samples. Optimization of the determination conditions was performed. In the case of DPV, Britton-Robinson buffer pH 7 was selected as the supporting electrolyte. In case of HPLC, mobile phase consisted of buffer pH 3:methanol (7:3, v/v); amperometric detection was performed in a wall-jet arrangement at +1.3 V detection potential. Determination limits of the methods are 1.3 μmol L^{-1} and 0.14 μmol L^{-1} for DPV and HPLC, respectively. The applicability of the methods was tested on the real tablet samples and model urine samples, in the latter case after the preliminary separation by the solid phase extraction.

Keywords: *Pharmaceutical; Voltammetry; Amperometry;*

P-0512

SUPRAMOLECULAR RECOGNITION OF BIOANALYTES

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Selective recognitions of biological important analytes under physiological conditions is a challenging task in supramolecular chemistry. Synthetic receptors that can achieve such tasks are important as diagnostic tools in medicinal chemistry and molecular biology. Molecular receptors for biologically important analytes like pyrophosphate (PPi), Adenosine-5'-triphosphate (ATP) and saccharides were investigated. Zn(II)-based coordination complex with a pendant azo-functionality as the reporter group[1] and self-assembled polydiacetylene (PDA) based vesicular receptors[2] have been prepared for the selective recognition of the ATP and PPi in aqueous solution. This receptor could be used as a staining agent and could even be capable of distinguishing the Gram +ve, Gram -ve bacteria and yeast cells.[1b]

A two-component glucose sensing concept based on anionic fluorescent dye and boronic acid-appended bipyridinium salt was already formulated.[3] Boronic acid-appended new photo switchable azopyridinium and bis-viologen based receptors have been prepared for improved carbohydrate recognition in water. Many different classes of enzymes, including phosphatases, phosphorylases, mutases, transferases, hydrolases and isomerases are involved in carbohydrate transformation. Thus, going beyond saccharide sensing, our current focus is to develop new assays for carbohydrate-active enzymes in a non-destructive, continuous manner for an industrial application.[4]

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Keywords: *Supramolecular chemistry; Enzymes; Carbohydrates; Sensors; Fluorescent probes;*

P-0513

THE CORROSION BEHAVIOR OF IRON POWDER PIECES IN SALT SPRAY ENVIRONMENT

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This paper presents studies on the corrosion behavior in saline medium of iron powder samples, obtained by powder metallurgy. They have parallelopipedic shape with dimensions of 10x10x55 mm and 5x10x55 mm and were pressed at 200 MPa, 300 MPa and 400 MPa. The samples of iron powder, reinforced and not reinforced with alloyed steel yarns were subjected to corrosion in salt spray environment, observing their behavior for about 100 hours.

Some of the specimens tested were electrolytic galvanized with zinc-as anticorrosive protection method, this way it was possible to make a comparison between the behaviors of two types of pieces. Verifications were made for observing the appearance and corrosion manifestation during the time the samples were kept in salt spray enclosure, this was captured in images. There have been tried other types of metallic coatings, as they will be subjected to corrosion in salt spray.

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Keywords: *Corrosion; salt spray environment;*

P-0514

CORROSION BEHAVIOR OF SINTERED IRON PM PARTS

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This paper presents some preliminary research on corrosion behavior in acidic pollutant medium for some sintered composite materials based on iron. This composite material can be used in carrying car component parts (gear wheels, levers). For testing we used cylindrical specimens pressed at 200 MPa, 300 MPa and 400 MPa, having the matrix from powder named ANCORSTEEL 1000B, reinforced with alloyed steel yarns

Experimental samples were subjected to chemical and electrochemical corrosion in aqueous solutions of de H_2SO_4 1 M and HCl 0.5 M, 1 M, 1.5 M, 2 M, 2.5 M. The experimental results regarding the corrosion rate for electrochemical tests were represented by Tafel curves, using a potentiostat VOLTALAB 40; chemical tests were obtained by calculation of gravimetric parameters and corrosion parameters. Tests showed that material to analyze is strongly corroded in weak acid environments, as factors that influence this process being specified: temperature, porosity of samples (ranging from 15-20%) and concentration of used solutions. For this reason, this new composite material cannot be utilized without using anticorrosion protection methods.

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P-0515

ANTIOXIDANT ACTIVITY OF WATER EXTRACTS IN 7 SELECTED HERBS

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Herbs are used in many domains, including medicine, nutrition, flavouring, beverages, dyeing, repellents, fragrances, cosmetics and they are a rich source of polyphenols. Polyphenolic compounds are commonly found in both edible and inedible plants, and they have been reported to have multiple biological effects, including antioxidant activity. Typical phenolics that possess antioxidant activity are known to be mainly phenolic acids and flavonoids. Phenolic acids are a major class of phenolic compounds, widely occurring in the plant kingdom especially in fruits and vegetables.

Total equivalent antioxidant capacities (TEAC) and phenolic contents of 7 spices herbs grown in Czech republic were investigated. The total antioxidant capacity was estimated by the following methods: ABTS (2,2-azinobis-(3-ethylbenzthiazoline--6-sulfonic acid)), DPPH (1,1-diphenyl-2-picrylhydrazyl radical) and ferric reducing/antioxidant power (FRAP) expressedas TEAC. The influence of season, location of harvest and treatment of selected herbs was investigated.

Keywords: *phenolic compounds; herbs; antioxidant activity;*

P-0516

THE DETECTION OF NEW ANTIBIOTICS AND THEIR TRANSFORMATION PRODUCTS PRODUCED BY ADVANCED OXIDATION PROCESSES IN MODERN WASTE WATER TREATMENT IN COMPARISON TO BIOLOGICAL DEGRADATION

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Environmental studies focus on researching and assessing today's most common pharmaceuticals. Modern and last resort antibiotics used for the treatment of bacterial infections caused by multi resistant bacteria are not subject to recent environmental risk assessments since they are rarely used and not detected today. The goal of this study is to evaluate the effects of advanced oxidation processes techniques to the recent last resort-antibiotics Tigecycline, Linezolide, Daptomycine and the modern agents Rifaximin, Piperacillin and Doripenem. For the detection of the new substances and their transformation products UPLC-MS (Synapt) was used.

As an exemplary result of two different transformation products of one origin substance we found with the treatment of Piperacillin with UV-radiation and the combination of H_2O_2 and Ozone. The usage of UV-radiation caused a specific breaking point and the production of a dioxopiperazine, whereas another method produced a thiazol carbocyclic acid.

The treatment of Daptomycin demonstrated the different efficiency of the advanced oxidation processes: The UV-radiation was unable to break down the target compound within the 30 minutes treatment, whereas the UV+H_2O_2-treament showed a complete degradation in the 10 minutes sample. Ozone seems to be strongest oxidizing agent since no original substance is present in the 5 minutes sample in all methods containing ozone-treatment.

Another exemplary result is of great concern showing a very stable transformation product. Linezolid was completely degraded after a few minutes, but the generated transformation product was insensitive to the selected treatment and is still present in the 30-minutes sample. Until now we were not able to identify the molecule, in addition no information is known about its possible (eco-) toxicity or biodegradability in aqueous systems.

Currently the structures of some metabolites of the aerobic biodegradation are subject of research and will be presented.

P-0517

FLUORESCENCE-BASED OPTICAL FIBER ANALYZER FOR DETERMINATION OF CATECHOLAMINES

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This work proposes an optical fibre (OF) analyzer for sensitive determination of catecholamines (dopamine, norepinephrine and epinephrine) in biological samples by induced fluorescence. The analytical set-up includes a chromatographic column for catecholamine separation, and a fluorescence-based OF detection (FOF-analyzer). The proposed methodology showed an adequate analytical performance for the determination of the above mentioned catecholamines in actual samples of human urine. The analytical performance of the FOF-analyzer was investigated against the high performance liquid chromatography – electrochemical detection (HPLC-ED) method. The FOF-analyzer showed lower detection limits and larger linear ranges for determination of dopamine, norepinephrine and epinephrine than the HPLC-ED and other methodologies such as HPLC-fluorescence. These advantages combined with the compact design, low-scale instrumentation, and effective cost of analysis makes this system a viable alternative to the existing methodologies for the determination of catecholamines in clinical samples.

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Keywords: *fluorescence; biosensors; liquid chromatography;*

P-0518

DETERMINATION OF CADMIUM AND LEAD IN THE PPB RANGE BY ATOMIC ABSORPTION

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In this study, a method is developed for the determination of cadmium and lead from fresh waters by flame atomic absorption spectroscopy (FAAS) after preconcentration by solvent extraction using Dithizone-ammonium pyrrolidine dithiocarbamate (APDC)-chloroform and compared to two other systems: APPC-chloroform and Dithizone-chloroform. Recovery values obtained in the preliminary studies after 20 fold preconcentration for lead and cadmium showed that the APDC-Dithizone system was in the same level or better when compared with the other two systems. The APDC-Dithizone system was then applied to ground waters. The Pb concentration was high enough to be determined by FAAS, but for Cd it was too low to be determined and GFAAS was tried for the determination of Cd. However, because of the poor condition of the instrument it became necessary to abandon the use of GFFAS and instead to increase the concentration factor. A 100 fold concentration factor was tested, combined with FAAS, with different concentration of Pb and Cd. The minimum measurable concentration for Cd was 0.2 ppb with average % recovery 99.1 ± 5.7 and the minimum measurable concentration for Pb was 1 ppb with average % recovery 102 ± 10.2.

Atom Trapping, slotted quartz tube (SQT) for increasing the sensitivity, was investigated for direct determination of analyte for FAAS. The sensitivity increased by 3 folds for Cd and Pb.

P-0519

NON-AQUEOUS CAPILLARY ELECTROPHORESIS APPLIED TO DETERMINATION OF ACID BASE DISSOCIATION CONSTANTS OF AZAHELICENES

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Azahelicenes represent unique helically chiral polyaromatic heterocycles[1], which are sparingly soluble or insoluble in water. Non-aqueous capillary electrophoresis (NACE) in methanolic background electrolytes (BGEs) with UV-absorption detection has been employed to determine acid-base dissociation constants (*pKa*) of ionogenic groups of selected azahelicenes. Acid-base dissociation constants of azahelicenes were calculated from the dependence of their effective electrophoretic mobilities on pH by nonlinear regression analysis. The effective mobilities were determined by NACE in methanolic BGEs within a wide pH range 2.1 – 11.2. NACE separations were performed in a home-made CE device equipped with UV-absorption detector operating at 206 nm and on a P/ACE MDQ instrument equipped with photodiode-array detector (Beckman Coulter, Fullerton, CA, USA) set at 206 nm. Experimental data were collected by chromatography station Clarity (Data-Apex, Prague, CR) and by software P/ACE MDQ System, version 32 Karat (Beckman Coulter), respectively. All results were handled by program Origin 6.1 (OriginLab, Northampton, MA, USA). Separations were performed in fused silica capillary (id/od = 50/375 μm, effective/total length 201/306 mm, outer polyimide coating, internally untreated). Applied voltage for separations was 12 kV (anode at the injection capillary end). Dimethyl sulfoxide was used as electroosmotic flow (EOF) marker[2, 3].

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Keywords: *Non-aqueous capillary electrophoresis; acid-base dissociation constants; azahelicenes;*

P-0520

SACCHARIDE SENSING AND MOLECULAR LOGIC AT THE FEW MOLECULE LEVEL OF THE REPORTING DYE

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The allosteric indicator displacement assay of a boronic acid appended viologen (BBV) and a fluorescent dye can detect saccharides in physiological conditions [1–4].

We investigated the interaction of the saccharide receptor and the reporter molecule with fluorescence correlation spectroscopy (FCS). This sensitive technique allows the detection of fluorescence signals from single/few molecules. FCS analyzes fluorescence intensity fluctuations with a confocal microscope mainly caused by local changes in concentration of the fluorescent dye.

On the basis of a nanomolar dye solution we showed the step-wise quenching of a fluorescent perylene diimide (PDI) with different BBV concentrations, followed by the fluorescence recovery with fructose (0 – 2 mM). Fluorescence transients were further used to calculate autocorrelation curves.

This switchable system allows to turn off the PDI fluorescence by adding the BBV-quencher and turn it on again via addition of fructose. The sensor forms a gate with the material implication (IMP) logic function, working with chemical input and generates a fluorescence output. The autocorrelation function yields the complementary notimplication function simultaneously. IMP is an extraordinary logic function from which all other Boolean-operators can be constructed, including only a trivial FALSE-operation [5]. Thus, IMP and FALSE operations are able to form adder and multiplicator logic circuits, based on the saccharide probe and fructose.

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Keywords: *Fluorescence spectroscopy; Sensors; fret; Carbohydrates;*

P-0521

ADSORPTION STUDY OF METAL IONS ON ELECTROCHEMICALLY SYNTHESIZED POLYANILINE

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The present work deals with the study of uptake behavior of Hg(II), Pb(II), Cd(II) and Zn(II) ions by Electrochemically synthesized Polyaniline using batch equilibration technique with both single and binary mixtures. The effect of the various parameters such as electrochemically synthesis method, physical oxidation state of the polymer, polymer thickness, solution pH and metal ion concentration on the adsorption, kinetics and efficiency were investigated.

The results showed avary broad concentration range of the metal ions from (0.2 to 10 mg/L) can be adsorbed on the polymer at pH = 5.8 (efficiently >98%). The adsorption capacity of the polymer to different concentrations of metal ions was evaluated as the milligram of metal ions by one gram of various forms of the polymer. The DC conductivity measurements were also employed on the solid polymer before and after adsorption of metal ions. The experimental adsorption date was fitted to different mathematical isotherms to estimate the binding constant of metal ions with the polymer in both single and mixed ion solutions.

P-0522

DETERMINATION OF IRON (II), IRON (III) AND TOTAL IRON IN SOME SS-THALASSEMIA PATIENTS USING DIFFERENT ANALYTICAL TECHNIQUES

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Iron as an essential element for living organisms, is oxygen transport and its role in oxidative-reductive reaction that utilize its alternative ferrous-ferric states. The biological importance of iron is widely attributed to its chemical properties, there are two oxidative forms, ferrous (Fe2+) and ferric (Fe3+) iron. Failure in this control result in anemia or iron overload. Thalassemia is a pediatric inherited disease, it is a type of chronic, microcytic anemia. It is gene-linked disease that can cause serious health problems because it can lead to the destruction of red blood cells. There are many well-known analytical methods for determination of iron (II) and iron (III). A mong these methods: gravimetric, titrimetric, potentiometric, conductometric, batch and flow – injection spectrophotometric methods. In the present study, two batch spectrophotometric, atomic absorption spectrometric and biolabo kit methods have been used for determination of iron (II), iron (III) and total iron. The present methods have the advantages of high sensitivity, low cost reagent, low operation cost, simplicity, speed and their applications for determination of iron (II) and iron (III) in some serum samples of normal human and β-thallasemia patients in Erbil city.

For the first time especially in Erbil city attempts were made to use zero, first and second derivative spectra to identify the serum samples of some β-thallasemia patients from the normal human serum samples due to the appearance and resolution of peaks in both cases.

Keywords: *Determination; Iron; ß-Thalassemia Patients; Analytical Techniques;*

P-0523

DEVELOPMENT OF NEW COLORIMETRIC REDOX INDICATORS FOR NADH VISUALIZATION

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Nicotinamide adenine dinucleotide/reduced nicotinamide adenine dinucleotide (NAD+/NADH) plays an important role as cofactor in numerous biocatalized processes, including energy metabolism, mitochondrial responses, immunological functions, aging and cell death. Particularly, the NAD+/NADH couple acts as the cofactor taking part in more than 300 dehydrogenase enzymatic reactions. Intracellular NADH also can serve as a natural biomarker for cellular redox reactions, a myriad of metabolic activities, and mitochondrial anomalies under different pathophysiological conditions. Consequently, numerous strategies have been proposed for NADH detection, including fluorescence imaging, enzymatic assay, high-performance liquid chromatography, electrospray ionization mass spectrometry, capillary electrophoresis, and electrochemical assay.[1] Under certain conditions, a colorimetric methodology may be preferred. For example, colorimetric assays are not sensitive to autofluorescence background, do not require complex instruments and demonstrate high sensitivities.[2] However existing redox indicators have multiple disadvantages: limits in UV and green range of light, poor solubility in water, low reactivity, lability to UV-light, water and oxygen.

Quinones have been known as representative organic electron acceptors for NADH oxidation due to their strong oxidizing ability as well as stability of the reduced species. It was found that UV-vis spectrum of quinone derivatives after NADH reduction exhibit absorptions in the longer-wavelength region.[3] With these in mind, we have decided to design new derivatives and analogues of quinones and test them for NADH visualization.

The NADH reduction of new quinone-type electron acceptors was seen by naked eye and monitored by UV-vis extinction spectra. Design, synthesis and UV-vis properties of several new indicators for NADH detection will be discussed.

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Keywords: *Redox chemistry; Biosensors; Dyes/Pigments; Cofactors; Quinones;*

P-0524

SIMULTANEOUS ANALYSIS OF CIRCULATING 25-HYDROXY-VITAMIN D3, 25-HYDROXY-VITAMIN D2, CAROTENOIDS, RETINOIDS, TOCOPHEROLS, AND OXIDIZED AND REDUCED COENZYME Q10 BY HPLC WITH PHOTO DIODE-ARRAY DETECTION USING C18 AND C30 COLUMNS ALONE OR IN COMBINATION

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Modern epidemiological and clinical studies commonly require high-throughput analyses that provide multiple biomarkers from a small volume, single blood specimen. Essential circulating lipid-soluble compounds play important roles in health and disease prevention and can, therefore, serve as useful biomarkers. We sought to develop a simple, fast, affordable, and highly accurate HPLC assay with diode array detection (DAD) that simultaneously measured all circulating lipid-soluble compounds.

In our study, 25-hydroxy vitamin D_2 and D_3, retinol, alpha-, beta-, gamma-, and delta-tocopherol, all major carotenoids including their isomers, and ubiquinol-10 and ubiquinone-10 were accurately quantitated in a single chromatographic run using **a**) a C18 column alone; **b**) a C30 column alone; or **c**) C18 and C30 columns connected in series. After several modifications, we refined our methods to resolve all analytes within 45–90 minutes or fewer analytes within 10 minutes.

The C18 alone excellently separated all major analytes but insufficiently resolved the vitamin D metabolites, lycopene isomers, and resulted in co-elution of lutein with zeaxanthin and beta- with gamma-tocopherol. The C30 alone was superior at separating the carotenoid isomers and beta- from gamma-tocopherol, but failed to resolve carotenoids from Q10 compounds. Connecting C18 and C30 in series with a DAD between and after the columns resulted in accurate quantitation of all analytes, however, was unacceptably long (90 minutes) due to the very low flow rate requirement imposed by back pressure limitations. Connecting C18 and C30 in series with only one DAD after the C30 column also resulted in carotenoid- Q10 interferences, but was remedied by adding a 6-port valve between the columns, which permitted resolution of all analytes in 45 minutes with a possible shortening of 15–20 minutes depending on the analytes included. In summary, our proposed methods can be custom designed to meet the needs of individual projects depending on analyte requirements.

Keywords: *Analytical Methods; Liquid Chromatography; UV/Vis Spectroscopy;*

P-0525

UTILIZATION AND OPTIMIZATION OF EXTRACTION BY ULTRASONIC PROBE FOR GAS CHROMATOGRAPHIC/MASS SPECTROMETRIC ANALYSIS OF PROPELLANT COMPONENTS

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Analysis of explosives, mainly smokeless powders and explosives mixtures, is an integral part of the production of explosives, fulminating compounds or propellants. Nowadays, chromatographic methods are used for these analyses, for example high performance liquid chromatography with ultraviolet detection (HPLC/UV). Modern methods and classical methods of propellant analysis (titration, gravimetry) require sample preparation to analysis. It means that target analytes have to be isolated from sample for their analysis. Isolation step of propellant analysis includes extraction methods usually. The extraction method is always selected according to the matrix of a sample and kind of sample. Conventional method for preparation of propellant samples and explosives samples is Soxhlet extraction with dichloromethane or diethyl ether as extraction agent.

A method for ultrasonic extraction by ultrasonic probe of nitroglycerin, triphenyl amine and acetyl tributhyl citrate presented in double-base propellant samples following by the gas chromatography/mass spectrometry analysis was developed. A central composite design of the experiments and response surface modeling was used for optimization of the time, amplitude and sample amount. The dichloromethane was used as the extractant solvent. The optimal extraction conditions with respect to the maximum yield of the lowest abundant compound triphenyl amine were found at the 20 min extraction time, 35 % amplitude of ultrasonic waves and 2.5 g of the propellant sample. The results obtained under optimal conditions were compared with the results achieved with validated Soxhlet extraction method. The extraction yield for acetyl tributhyl citrate using both extraction methods was comparable; however, the yield of extraction by ultrasonic probe of nitroglycerin and triphenyl amine was lower than using Soxhlet extraction.

Keywords: *smokeless powder; extraction by ultrasonic probe; optimization; Soxhlet extraction; gas chromatography/mass spectrometry;*

P-0526

INVESTIGATION WATER-SOLUBLE AND LIPOSOLUBLE ANTIOXIDANTS USING METAL COMPLEXES

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Currently, the great attention is given to development of methods for determination of antioxidant activity (AOA). The most accessible and express method for determining of AOA are electrochemical methods.

The simple potentiometric method determination of AOA has been proposed. It is based on the interaction of antioxidants of the sample with the mediator system $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$[1-2]. However, the using of water-soluble complexes does impossible to use this method in organic solvents for the study of liposoluble compounds with antioxidant properties, which are the most important class of antioxidants. The approach which based on the using of metal-organic compounds in organic solvents as a redox-mediators was offered. Ferrocene and hetaryl-ferrocenes systems and their oxygenized salts have been investigated. The using of these systems is limited to a small stability of salts ferrocenium in organic solvents.

A new approach based on measurement of the electrode potential after the chemical reaction between the antioxidants of the sample and the oxidized form of the metal complex. It is leads to reducing of number of measurement steps. The use of singular form of the reagent can significantly increase the number of reagents used and the range of the objects in different solvents. The validity of the proposed approach is confirmed by the "introduced-found" method in the case the well-known interactions model of $K_3[Fe(CN)_6]$ and of water-soluble antioxidants. Diketonates of metals, particularly iron (III), showed the greatest perspective in use in organic solvents. Experiments with this complex were carried out on models of phenolic antioxidants in acetonitrile and ethyl alcohol.

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Keywords: *Antioxidant; Metal complexes; Potentiometry;*

P-0527

A NEW METHOD FOR A COMPLETE 3-D ANALYSIS OF ORGANOMETALLICS IN A FEW HOURS

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Single crystal X-ray diffraction (SC-XRD) is a powerful tool for synthetic chemists. It is the most unambiguous method to accomplish a '3D analysis' in the course of one single experiment. This complements and extends information obtained using other methods, such as NMR, IR, UV, MS, ORD and many more. The '3D analysis' obtained using SC-XRD reveals constitution, configuration and conformation, with accurate information about bond lengths, bond angles and the arrangement of the molecules within the sample. Unfortunately, synthetic chemists often had limited access to SC-XRD since they had to send their samples to external X-ray facilities. These instruments require trained specialists, already for collecting the required data. This made the 3D analysis a time consuming tedious undertaking in the past.

Now, the SMART X2S greatly simplifies the availability of SC-XRD in your laboratory. The SMART X2S desktop system helps controlling your synthesis by true walk away automation. Recently solved structures ($UC_{45}H_{22}N_2O_5$; $IrC_{30}H_{20}N_2Cl$) will be discussed to highlight the system's main features.

Keywords: *Bruker; SMART X2S; single crystal diffraction;*

P-0528

ACTIVITY OF DISINFECTANT SOLUTIONS

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Knowing antiseptic activity of chemical disinfectant substances has a great practical value. It is evidential that there is the need for defining standard technique for quantitative determination of bactericidal activity of chemical disinfectant substances. Solution of phenol (5%) was considered as referent standard for evaluation of efficacy of disinfectant aqueous solutions. On the other side the methods for evaluation of antiseptic activity of disinfectant aqueous solutions are microbiological.

The aim of this study is to develop a new empirical coefficient which is capable to express the various physicochemical properties of disinfectant solutions on bactericidal activity. This parameter (Disinfection Activity Coefficient of Solution - DACS) has to express capability for comparison and prediction of disinfectant activity. The DACS index, which is the sum of four terms (fluidity, surface tension, redox potential and osmolality) is in good correlation with the activity at different disinfectant aqueous solutions. The DACS index can be calculated using additive and statistical models. Statistical model is adequate for evaluation of different disinfectant solutions because of better expressing the bactericidal activity then additive model. For analyze of various dilutions of one disinfectant there is no significant difference between this two models. The usefulness of DACS is demonstrated for analyze of bactericidal activities on different disinfectant solutions containing boric acid, chlorhexidne, chlorhexidine with cetrimide, chloroxylenol, chlorophen, eosin, hydrogen peroxide, phenyl mercury borate, povidon-iodine, thiomersal, tosilchloramide and phenol. Results for bactericidal activities obtained from microbiological tests on *Staphylococcus aureus* were compared with activities predicted by DACS. As the conclusion, it is considered good correlation between experimental and calculated values for bactericidal activity.

Keywords: *disinfectant; bactericidal activity;*

P-0529

ELECTROCHEMICAL PROPERTIES OF CUPPER(II)-GLYCINE COMPLEX

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The diversity of inorganic compounds and their applications in medicine encompass cancer chemotherapy, arthritis, antimicrobial agents, and many others. Metal complexes of biologically important ligands are sometimes more effective than the free ligands. Cu(II), Ni(II), Co(II) and Zn(II) metal cations are recognized as essential elements that are distributed in biological systems including cells and body fluids. Also, copper exists in nuclei and plays a key role in determining DNA quaternary structure. There are a few studies on the electrochemical investigation of glcyinato complexes of metal cations. In this study Cupper(II)-Glycine complex was synthesized and characterized firstly and then the electrochemical behaviour of this complex hes been investigated by the use of several electrochemical methods in DMSO on glassy carbon electrode. The number of electron transferred (n) and diffusion coefficient (D) in the reduction of the complex were calculated by cyclic voltammetric and chronoamperometric results for both the complex and ferrocene with ultramicro electrode. The mechanism confirmed by comparing experimental cyclic voltammogram to the theoretical one drawn with simulation software. On the other hand the standard rate constant (k_s) and transfer coefficient (a) of the electrochemical reaction were also calculated from this simulation study.

Keywords: *Cupper(II)-Glycine complex; Transititon metal complexes; Electroanalytical chemistry; ultramicroelectrode; cyclic voltammetry;*

P-0530

ELECTROCHEMICAL BEHAVIOUR OF COBALT(II)-GLYCINE COMPLEX

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The electrochemical properties of Cobalt(II)-Glycine complex has been investigated by the use of several electrochemical methods in DMSO on glassy carbon electrode. Metal complexes of biologically important ligands are sometimes more effective than the free ligands. Co (II), Ni(II), Cu(II) and Zn(II) metal cations are recognized as essential elements that are distributed in biological systems including cells and body fluids. It is well documented that heterocyclic compounds play a significant role in many biological systems, especially N-donor ligand systems being a component of several vitamins and drugs. The metal-binding properties of carbohydrates have been shown to be of fundamental importance in many biochemical processes such as the transport and storage of metals, the function and regulation of metalloenzymes, the mechanism of action of metal –containing pharmaceuticals, and toxic metal metabolism. There are a few studies on the electrochemical investigation of glcyinato complexes of metal cations. In this study Cobalt(II)-Glycine complex was synthesized and characterized firstly and then the electrochemical reduction of this complex was investigated by several techniques. The number of electron transferred was calculated by the use of ultramicro electrode. The reversibility tests were applied to elucidate the reaction mechanism. The mechanism also confirmed by simulation studies. k_s and a values were calculated from simulation studies.

Keywords: *Cobalt(II)-Glycine complex; Transititon metal complexes; Chronoamperometry; Electroanalytical chemistry; Electrochemical simulation;*

P-0531

LABEL-FREE ELECTROCHEMICAL APTASENSORS WITH SUB-FEMTOMOLAR DETECTION LIMIT TOWARDS THROMBIN

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Immunosensors based on aptamers as a new molecular recognition element have received great attention due to aptamer's specific binding to a wide range of target molecules including proteins, enzymes, and even small organic molecules. To achieve more robust utility for aptamer sensors, it is particularly important to develop label-free detection methods. Several strategies of label-free immunoassay have been demonstrated by employing electrochemical impedance spectroscopy (EIS), quartz crystal microbalance (QCM), surface plasmon resonance (SPR) spectroscopy, and atomic force microscope (AFM) cantilever. Herein, we report on a new approach to design an electrochemical aptamer sensor for a simple, label-free detection of thrombin as a model target protein. The thiolated thrombin-binding aptamer (TBA) is immobilized on the gold electrode surface based on well-known gold-thiol chemistry, followed by immobilization of 1-mercapto-6-hexanol on the electrode to prevent non-specific binding of thrombin and other proteins. The specific binding of thrombin with TBA leads to changes in the interfacial electron transfer of electrochemically active probes (e.g., ferrocene and ferricyanide). Indeed, the surface coverage with thrombin prohibits the access of electrochemically active probes to the electrode surface. To amplify such a blocking effect associated with thrombin-TBA complex formation, we employ silica nanoparticles as a scaffold to design "macromolecular electroactive probes." The ferrocene-modified silica nanoparticles are synthesized by carbodiimide coupling chemistry between ferrocene-carboxylic acid and amines functionalized on the silica surface. The effects of particle size (7 to 14 nm), surface charge, and density of ferrocene on the silica surface on sensor performance (e.g., sensitivity and detection limit) will be discussed.

Keywords: *Aptasensor; Label-free; Ferrocene-modified silica nanoparticle; Electrochemical sensing; Thrombin;*

P-0532

QUANTITATIVE DETERMINATION OF LANSOPRAZOLE AND ITS IMPURITIES BY HPLC

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Lansoprazole, 2-[(3-methyl-4-(2,2,2-trifluoroethoxy) pyridin-2-yl) methylsulfinyl] -1*H*-benzoimidazole, is a proton-pump inhibitor (PPI) which prevents the stomach from producing gastric acid. The aim of the study is to seperate and determine Lansoprazole and its impurities, Lansoprazole sulphide, Lansoprazole sulphone, Lansoprazole N-oxide, by HPLC.

A precise, accurate, sensitive and fast model is described for quantitative determination of these compounds in pharmaceutical forms. A reversed phase C18 column (5 µm, 150 mm x 4.60 mm, i.d.) and o-phosphoric acid: water: methanol, 5:245:750, v/v, mobile phase were used. The flow rate was 1.0 mL/min and 255 nm was selected for UV detection wavelength. The recoveries were in the range of 98.7-100.6% for Lansoprazole. The results for Lansoprazole in tablets were in agreement with the labeled quantities.

Keywords: *Analytical Methods; Liquid Chromatography;*

P-0533

CYCLIC VOLTAMMETRIC STUDY OF DIFFUSION COEFFICIENTS OF RADICAL IONS AND THE CORRESPONDING NEUTRAL MOLECULES IN ROOM TEMPERATURE IONIC LIQUIDS

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The ratio D_{ox}/D_{red}, where D_{ox} and D_{red} are the diffusion coefficients of the electrogenerated radical anion and of the corresponding neutral molecule, respectively, is commonly found to be one in organic solvents. Sometimes, this is not the case in ionic liquids, as shown by Compton et al[1, 2] who reported that the diffusion coefficients of ferrocenium cation, cobaltocenium cation and $TMPPD^{+\cdot}$(TMPPD: N,N,N',N'-tetramethyl-p-phenylenediamine) are smaller than those of the reduced forms. Similar results have been obtained by Hapiot et al for aromatic nitro compounds[3] and ferrocene derivative[4]. Therefore, an incorrect assumption about the ratio D_{ox}/D_{red} leads to errors in calculation of the heterogeneous electron transfer rate constant.

In this work, diffusion coefficients of an electroactive neutral substance, tetracyanoethylene (TCNE) and of the potassium salt of the corresponding radical anion have been measured by cyclic voltammetry in five different room temperature ionic liquids: $emim^+BF_4^-$, $bmim^+PF_6^-$, $bmim^+BF_4^-$, $omim^+PF_6^-$, $omim^+BF_4^-$. The values of the diffusion coefficients depend on the inverse viscosity for all ionic liquids. The diffusion coefficients of $TCNE^{-\cdot}$ are lower than those of TCNE whichever the medium. The results found for the diffusion coefficients in these ionic liquids are used to determine the heterogeneous electron transfer rate constants.

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Keywords: *Cyclic voltammetry; Ionic liquids; Electrochemistry; Electron transfer;*

P-0534

STUDY OF IONIZATION OF OPIATES IN URINE SAMPLES FOR MASS SPECTROMETRIC ANALYSIS

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Opiates are substances which are naturally occurring in opium or semi-synthetic substances. They exhibit narcotic effects and relieve the pain but also create psychological a physical dependence. They cause mood swings (euphoria, sedation), tremor, insomnia etc. In this study, ionization of three opiate representative (morphine, 6-acetylmorphine and morphine-3b-D--glucuronide) using electrospray and nanoelectrospray was studied.

Experiments were performed using LCQDUO Ion Trap (Thermo Finnigan USA) equipped with two ion sources – electrospray (ESI) and nanoelectrospray (nanoESI). Their tolerance to salt in samples was evaluated. Nanoelectrospray showed a higher tolerance and was used for urine sample analysis. Human urine was spiked by standards; deuterated substances were used as internal standards. Solid phase extraction was used for sample purification and analyte preconcentration. SPE columns Waters OASIS MCX Cartridge were used. Phosphate buffer (pH = 8,5) for conditioning, acetate buffer (pH = 4) elution of impurities and methanol:water 98:2 for analyte elution. Eluates were evaporated to dryness and dissolved in 100ul of methanol:water:HCOOH 50:49:1 (v/v). These samples were analyzed by nanoESI without chromatographic separation. Morphine and 6-acetylmorphine can be detected in urine at level 0,2 mg/l.

P-0535

A BIOMIMETIC SENSOR SURFACE TO DETECT ANTI-BETA2-GLYCOPROTEIN-I ANTIBODIES AS A MARKER FOR ANTIPHOSPHOLIPID SYNDROME

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A biomimetic sensor has been developed, that allows for quantification of autoantibodies related to the antiphospholipid syndrome (APS). Autoantibodies directed against the β2-glycoprotein-I (β2GP-I) are known as the best markers for diagnosis of APS, however, detection of such antibodies is still a challenge. The epitopes of β2GP-I are exposed upon binding to negatively charged membranes. The surface of the sensor chips was therefore modified with such type of membranes, on which β2GP-I molecules were subsequently immobilized as recognition elements. Using the label-free method, reflectometric interference spectroscopy, it was possible to quantify anti-β2GPI antibodies and to calibrate the sensor chip in buffer. A mild regeneration procedure allows for many consecutive measurements without stripping off the membrane in between.

Keywords: *Reflectometric interference spectroscopy (RIfS); Biosensors; Antibodies; Membranes; Liposomes;*

P-0536

A COMPARISON OF MALDI MATRICES BASED ON LITHIUM SALTS FOR ANALYSIS OF HYDROCARBONS AND WAX ESTERS

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Matrix assisted laser desorption/ionization (MALDI) is an effective method for a rapid characterization of lipid mixtures. Data obtained from MALDI spectra are useful for quick comparison of the samples composition or chemotaxonomic purposes. MALDI is a suitable method for analysis of all classes of lipids from complex polar lipids to simple and completely non-polar lipids. The processes taking place in MALDI are rather complicated and have not been fully understood yet. The choice of MALDI matrix depends on the analyte structure. For neutral lipids only few effective matrices have been described. In this work several new matrices based on lithium salts of organic aromatic acids (lithium 2,5-dihydroxytereftalate, lithium 2,5-dimethoxybenzoate, lithium α-cyano-4-hydroxycinnamate, lithium sinapate, lithium benzoate, lithium salicylate, lithium vanillate) were tested as potential matrices for MALDI-MS analysis of hydrocarbons (HCs) and wax esters (WEs). As shown previously, the ionization of neutral lipids occurs via attachment of lithium cation, which yields $[M + Li]^+$ adducts. The new matrices were evaluated and compared with lithium 2,5-dihydroxybenzoate, which is a proven matrix for MALDI analysis of lipids. Several parameters, including laser power, sample deposition protocols and matrix to analyte ratio were optimized for each matrix. The signal intensity and repeatability was compared using standards (stearyl behenate, n-triacontane). In addition, the nature of matrix ions and their range on *m/z* scale, absorbance at laser wavelength 337 nm and solubility in various solvents were studied. The morphology of the sample deposits were discussed based on images taken from a scanning electron microscope. The applicability of the matrices was tested on natural samples (WEs from bees wax and plant waxes, insect cuticular HCs). The best results were achieved with lithium vanillate. It was found that effective matrices contain hydroxyl group. A correlation between efficiency and a content of crystal water in the matrix crystals was also observed.

Acknowledgement: *This work was supported by Czech Science Foundation GACR (Project No. 203/09/0139) and the Academy of Sciences of the Czech Republic (Project RVO: 61388963).*

Keywords: *MALDI matrices; wax esters; hydrocarbons;*

P-0537

VCD STUDY OF 1-PHENYLETHYL-N,N-DIMETHYL-N-ALKYL AMMONIUM BROMIDE

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The chiral derivatives of 1-phenylethyl-N,N-dimethyl--N-alkyl ammonium bromide are agents from group of α-phenylethylamine, which is a well known and often used chiral auxiliary, e.g. in chiral ligands for asymmetric catalysis, resolving agent or in organocatalysts. Ammonium bromides are potentiall agents for accelerated penetration of chiral drugs through the skin.

The compounds were investigated using vibrational circular dichroism (VCD) spectroscopy. Experimental spectra of alkyl ammonium bromides (alkyl R = 0, 8, 10, 12, 14, 16, 18 carbon atoms) were measured in deuterated methanol in spectral region of 1800 – 1200 cm^{-1}. Spectra were interpreted using a combination with ab initio calculations based on density functional theory.

Results relevant to the conformation and absolute configuration will be discussed.

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Keywords: *Circular dichroism; Conformation analysis; Ab initio calculations; Chiral auxiliaries;*

P-0538

PRESSURIZED HOT WATER EXTRACTION OF CAPSAICIN AND DIHYDROCAPSAICIN FROM CHILLI PEPPERS

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Pressurised hot water extraction (PHWE) use water as an extraction medium and belongs to one of the field called „green chemistry'. Water is non-flammable, non-toxic, readily available and cheap and as solvent environmentally benign. The change in its physic-chemical properties at elevated temperatures and pressures enhances its usefulness. Pressurized hot water has been used to replace conventional organic solvents in extraction process. Optimized parameters are in particular temperature, pressure, extraction time and amount of sample. PHWE was used for extraction of capsaicin (CPA) and dihydrocapsaicin (DHC) in seasoning (chilli peppers). Like reference method to PHWE was chosen ultrasonication extraction. HPLC/UV/MS was used for determination of target analytes.

Keywords: *PHWE; capsaicin; dihydrocapsaicin; HPLC/UV/MS;*

P-0539

THE EFFECT OF O-SUBSTITUENT ON MASS SPECTRUMS OF SCHIFF BASES PREPARED FROM SALICYALDEHYDE

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As is known, Schiff bases are ligands used in coordination chemistry by P.Pfeiffer in early 1930s [1]. Despite the old age of the material class, there has not been many studies on the mass spectra of schiff bases reported in the literature [2]. In this study asymmetric and symmetric salicylaldymines were ionized by 20, 40, 60, 100, 120 and 140 eV electrons using Direct Inlet and obtained m/z values were evaluated. The schiff bases that were used are o, m, p-substituted N-phenyl salicylaldimines and Bis-N-N'(salicylidene)-diamino alkanes. Especially in mass spectra of o-substituted Schiff bases, the formation of H_2O, HF, HCl, HBr, HI or CH_3OH by phenolic hydrogen and o-substituent was observed and the remaining mass was noted as the main peak subsequent to the leaving of these groups. It was also seen that HBr and HI species, formed by bromine and iodine substituents, get attached to the molecule. At this point, it is clear that the additions of HBr and HI do not occur by an acid-base reaction mechanism because the found mass values are equal to the sum of the mass of the Schiff base molecule injected to the DI probe and the mass of one HBr or HI molecule.

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Keywords: *Schiff base; DI; Mass spectrum; o- effect;*

P-0540

CHARACTERIZATION OF IVERMECTIN AND ITS METABOLITES USING UHPLC/MS/MS

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Ivermectin (IVE) is an anti-parasitic drug with a broad-spectrum of usage in the veterinary and human medicine. It belongs to a macrocyclic lacton drug group called avermectins that is effectively applied in cases of nematode, arthropod and especially onchocerciasis infections. In mammals, IVE is metabolized mainly in liver, where hydroxylated and demethylated metabolites and sulphate conjugates are formed, but these processes are not extensive. The elimination of the parent form and its metabolites is ensured in 90% by the fecal and bilinary system. In our work, IVE was incubated with rat hepatocytes and microsomes. Subsequently, the solid-phase extraction of microsomal and hepatocyte incubation mixtures was performed. Moreover, human microsomal samples were obtained from *in vitro* experiments. The comparison of incubated samples with placebo experiments simplified the identification of metabolites. Studied samples were analyzed using optimized ultra-high performance liquid chromatography with electrospray ionization tandem mass spectrometry providing the information about IVE microsomal and hepatic biotransformation pathways. Structural changes of particular phase I and II metabolites were suggested based on high mass accuracy measurements in the full scan and tandem mass spectrometry modes using QqTOF analyzer.

Acknowledgement: *This work was supported by grant project P502/10/0217 (Czech Science Foundation).*

Keywords: *anthelmintic drug; ivermectin; tandem mass spectrometry; ultra high performance liquid chromatography;*

P-0541

CORRELATION OF X-RAY FLUORESENCE SPECTRA, SCANNING ELECTRON MICROSCOPE IMAGES AND BATCH REMOVAL EFFICIENCY OF LOW COST ADSORBERS IN THE REMOVAL PB(II)FROM WASTEWATERS

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X-ray fluorescence (XRF) spectra and scanning electron microscope images (SEM) of low cost adsorbers were collected and correlated with their Pb(II) removal efficiencies. Adsorbers employed included white, red and yellow sands (United Arab Emirates), Hannon, Micawer and Aritain zeolites (Jordan), activated silica (Jordan) and commercial bentonite. Removal efficiencies of Pb(II) on the above surfaces were investigated at 25.0°C as a function of Pb(II) concentration and adsorbent dosage using the batch equilibrium method. These results were compared to those obtained with commercial silica and alumina. Bentonite was found to be the most efficient adsorber, 1.0 g of which being sufficient to completely remove Pb(II) ions from 0.100 dm^3 of a 100 ppm aqueous solution. Bentonite was followed by zeolites whose removal efficiency order was: Hannon > Aritain > Micawer. These were followed by UAE sand which followed the order: yellow > white > red. Finally, on the lower efficiency scale, the order observed was: activated silica > kaolin> silica~alumina. The removal efficiency of bentonite was nearly ten-fold that for the least efficient remover, silica or alumina. XRF spectra suggest that the high content in zeolites of the oxides of magnesium, iron and aluminum enhance their removal efficiency. SEM images allow for the correlation of the adsorber morphology to its adsorptive efficiency.

Keywords: *X-ray fluorescence;*

P-0542

SYNTHESIS OF CONDUCTING POLYMER/PT COMPOSITES – PT DEPOSITION AND MORPHOLOGY STUDY

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Conducting polymer/Pt (CP/Pt) composites are nowadays widely used for many applications. For example in microelectronics, catalysis and in chemical sensors. These composites found significant application in the field of fuel cells where they are considered to be an alternative catalyst support.

There are different ways of platinum particles deposition. In almost all published cases Pt is deposited from chloride ions containing precursors – $H_2[PtCl_6]$, $K_2[PtCl_6]$, $H_2[PtCl_4]$, $K_2[PtCl_4]$, $PtCl_4$. It is well known that chloride ions adsorb on platinum surface and the electrocatalytic activities of such particles can be influenced.

The aims of this study are: (i) to find suitable, chloride free and commercially available platinum compounds which can be used for CP/Pt composites synthesis, (ii) to study the influence of the precursor and deposition method on platinum particles morphology and (iii) to compare electrocatalytic activities of composites prepared from chloro- and nonchloro-precursors.

Composites based on polyaniline (PAni) and polypyrrole (PPy) were studied. The films were prepared electrochemically. Glassy carbon rotating disc electrode, area 0,196 cm^2, served as a support. PAni was synthesized using cycling voltammetry, PPy was prepared potentiostatically at the potential 1 V vs. SHE. Platinum particles were deposited galvanostatically and potentiostatically under different conditions from $K_2[PtCl_4]$, $K_2[Pt(ox)_2]$, $[Pt(NH_3)_4](NO_3)_2$ and $Pt(NO_3)_2$. The samples with different amounts of platinum were characterized by scanning electron microscopy and by means of image analysis. Subsequently the electrocatalytic activities of prepared samples for methanol oxidation reaction using cycling voltammetry were determined.

It was found that the only compounds from which the platinum can be deposited on the PAni and PPy films are $K_2[PtCl_4]$ and $K_2[Pt(ox)_2]$. The morphology of obtained Pt particles differs strongly. The precursors $[Pt(NH_3)_4](NO_3)_2$ and $Pt(NO_3)_2$ are not suitable for Pt depositin on CP films.

Keywords: *conducting polymer/platinum composites; platinum deposition;*

P-0543

INFLUENCE OF CHLORIDE IONS ON ELECTROCATALYTIC ACTIVITY OF CONDUCTING POLYMER/PT COMPOSITES

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Conducting polymer/Pt (CP/Pt) composites can be used in the fuel cells as an alternative electrode material. Platinum serves as an electrocatalyst and poisoning of its surface can lead to decrease of the fuel cell efficiency.

Despite the chloride ions sorption on platinum surface is well known effect, practically only the chlorocomplexes of platinum are used for CP/Pt synthesis. Together with fact that chlorides are common impurity in drinking water there is a risk of decrease of electrocatalytic activities of composites in FC applications. Yet the systematic study of this effect has not been done.

The aims of this study are to measure electrocatalytic activities of CP/Pt composites for methanol oxidation reaction (MOR) and for hydrogen oxidation reaction (HOR) and determine the influence of chloride ions on these activities.

Composites based on polyaniline (PAni) and polypyrrole (PPy) were studied. The films were prepared electrochemically. Glassy carbon rotating disc electrode, area 0,196 cm^2, served as a support. Platinum particles were deposited potenciostatically at the potential 0,1 V vs. SHE from $K_2[Pt(ox)_2]$, Pt loading 100 µg cm^{-2}. Subsequently the electrocatalytic activities for MOR and HOR under different chloride concentration were measured. The activities for MOR were measured using cyclic voltammetry, activities for HOR were obtained by Koutecky-Levich analysis of polarization curves.

It was found that chloride ions strongly decrease the electrocatalytic activity. Concentration of chloride anions 10^{-2} mol dm^{-3} leads to decrease of activity for HOR of about 50–70%. It was also found that the influence of the chloride ions on the HOR on the PPy/Pt composites is dependent on the electrode potential. The influence of the chloride ions on the MOR is even more pronounced, in the presence of above stated chloride ions concentration the platinum surface is almost completely blocked and the MOR doesn't take place.

Keywords: *conducting polymer/platinum composites; chloride poisoning;*

P-0544

APPLICATION OF ICP-AES METHOD FOR COMPOSITION DETERMINATION OF NICKEL SUPERALLOYS

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To control quality and composition of new Nickel superalloys we have developed test methods for the analysis of doping elements (Al, Co, Re, Ru, Ta, W, Cr, Mo, Ti, Nb) and impurities (La, B, Si, Ce, Y, Fe, Cu, Mn, P) by using ICP-AES method.

To choose acids for Ni alloys dissolving we have taken into account chemical properties of analysing elements:

- Si with HF forms volatile SiF_4, SiH_4; in mixture of HCl and HNO_3 silicon is precipitated into silica sol $(H_2SiO_3)_n$; silicon is washed away from the glass spray system of spectrometer; silicon is adsorbed on the teflon spray system;
- at dissolving in mixture of acids HCl, HNO_3 and HF without water aluminum forms poorly soluble fluoride AlF_3 at Al content more than 4 % wt;
- if Cr content is more than 15 %, Cr is passivated in HNO_3;
- at dissolving of carbon-bearing alloys chromium carbide solved completely only in HF;
- Ru forms volatile compounds;
- boron is washed away from the glass spray system;
- W, Nb, Ta, Mo is dissolved completely only in present of HF.

Therefore analysing elements were devided in two groups. For dissolving of La, B, Ce, Y, Fe, Cu, Mn, Si (up to 3 % wt) we chose mixture of chlorazotic acid and water in the ratio 1:2,5. Re, Ru, Ta, W, Mo, Ti, Nb, P, Cr, Al, Co, Si (more than 0,1 % wt) was dissolved in mixture of acid HCl, HNO_3 and HF. Alloy samples were dissolved by using microwave digestion system MARS5 for excluding losses. Investigations were carried out by using ICP-AES spectrometer Varian 730ES with axial system. The wavelengths were chosen for elements' analysis without interference.

Thus developed test methods considering abovementioned properties allow to determine elements with error 3 % in concentration ranges from 0,01 to 20 % wt.

Keywords: *Ni alloys; ICP-AES; test method;*

P-0545

AMPEROMETRIC NITRIC OXIDE AND OXYGEN GAS MICROSENSORS FOR MONITORING MYOCARDIAL ISCHEMIA AND REPERFUSION INJURY IN RAT HEART

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Endogenously produced nitric oxide (NO) has been studied extensively. It has a number of important physiological actions in the cardiovascular system. The heart generates NO from L-arginine and oxygen (O_2) by nitric oxide synthases (NOSs) which is present in the coronary endothelium, endocardial endothelium, and cardiac myocytes. Since NO endogenously generated has been implicated in the control of O_2 consumption, it may be essential to monitor O_2 levels during NO measurement in physiological milieu. Electrochemical gas sensors possess several major advantages, including high sensitivity, high spatial and temporal resolution, and simple miniaturization for *in vivo* measurement. Recently, amperometric NO and O_2 gas sensors have been extensively employed to determine NO and O_2 concentrations in biological systems. However, the electrooxidation of NO requires a comparatively high working potential (+0.8 V vs. Ag/AgCl); thus, selective detection of NO is difficult due to other readily oxidizable interfering species (e.g., nitrite, ascorbic acid, uric acid, and acetaminophen). Another problem associated with biological measurements is biofouling (initiated by protein adsorption) at the electrode surface. To improve both the selectivity and protein adsorption, the working electrode surface is modified with a xerogel membrane. It is well-known that amorphous, hydrophobic perfluoropolymers (e.g., Teflon) are highly permeable to various gaseous species including NO and O_2. Herein we devlop amperometric NO and O_2microsensors modified with perfluorinated xerogel-derived gas permeable membrane, exhibiting dramatically improved selectivity and biocompatibility, while maintaining high permeability toward NO and O_2. Furthermore, we demonstrate the utility of the perfluorinated xerogel-modified microsensor to monitor NO and O_2 concentrations in myocardial ischemia and reperfusion injury in a rat model *in vivo*. The measurement reflects co-dynamic relationships between NO and O_2 contents in rat heart.

Keywords: *Amperometric gas sensor; Nitric oxide; Oxygen; Myocardial ischemia/reperfusion injury; Rat heart model;*

P-0546

STUDY OF SYSTEMS CONTAINING SILVER NANOPARTICLES MODIFIED BY CYSTEINE ENANTIOMERS

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In this study we report a behavior of systems containing silver nanoparticles and L- or D-cysteine. Silver nanoparticles, approximately 45 nm in diameter, were prepared by citrate reduction of silver nitrate solution. Optical activity was induced via post-synthetic modification of nanoparticles surface with L- or D-cysteine. Influence of cysteine concentration, pH, and time on these systems was studied. Mixtures were mainly characterized by electronic circular dichroism (ECD), but UV-Vis absorption spectroscopy and surface enhanced Raman scattering (SERS) measurements were also used. Results of SERS showed that cysteine was bonded on surface of nanoparticles and we were able to detect it in concentration up to 5.10^{-9} mol L^{-1}. Also ECD spectroscopy revealed the influence of cysteine concentration on ECD spectra.

Keywords: *Circular dichroism; Silver nanoparticles; Chirality;*

P-0547

VOLTAMMETRIC DETERMINATION OF ORNIDAZOLE BY MEANS OF A MERCURY MENISCUS MODIFIED SILVER SOLID AMALGAM ELECTRODE

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In therapeutic research, nitro compounds have become an important group of drugs with multiple pharmacological activities and, on the other hand, a nitro group is frequently associated with increased mutagenicity and carcinogenicity of the substance. Ornidazole, a derivative of nitroimidazole, is used as an antibacterial and antiprotozoal drug.

This work is focused on optimization and application of voltammetric techniques (direct current voltammetry (DCV) and differential pulse voltammetry (DPV)) for the determination of ornidazole using a mercury meniscus modified silver solid amalgam electrode (m-AgSAE). This electrode offers good repeatability and renewability of its surface, it represents cheaper, more user- and environmental-friendly alternative to the hanging mercury drop electrode (HMDE). The optimum conditions for the determination of ornidazole in the concentration range from $2 \cdot 10^{-7}$ mol/L to $1 \cdot 10^{-4}$ mol/L were found in the medium of Britton–Robinson buffer of pH 8.0; the limits of quantification (L_Qs) were found to be $1.5 \cdot 10^{-7}$ mol/L for DCV and $2.3 \cdot 10^{-7}$ mol/L for DPV.

The practical applicability of the newly developed DPV methodology was verified for the direct determination of ornidazole in model samples of drinking and river water, with $L_Q\text{s} \approx 2.4 \cdot 10^{-7}$ mol/L and $2.0 \cdot 10^{-7}$ mol/L reached in drinking a river water, respectively.

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Keywords: *Electrochemistry; Voltammetry; Analytical methods; Amalgams;*

P-0548

CAPILLARY ELECTROPHORESIS ASSAY FOR DETERMINATION OF BETA-N-ACETYLHEXOSAMINIDASE ACTIVITY

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Determination of enzyme activity is vital for basic and applied research in biochemistry and molecular biology. Apart from that, it can be used for the diagnosis of serious diseases, such as cancer, that causes changes in the enzyme activity in body fluids. This work focuses on the development of capillary electrophoresis methods for determination of substrates and products of the *β-N*-acetylhexosaminidase enzyme. The enzyme in question plays an important role in the cell regeneration, hyphenation and septa formation in fungi and, therefore, it is of a great research interest. *β-N*-acetylhexosaminidase is also present in human, where it is involved in degradation processes. Mutations of this enzyme can cause fatal inborn errors known as Tay-Sachs and Sandhoff disease.

A reliable capillary electrophoresis method enabling the monitoring of hydrolysis of *N,N',N''*-triacetylchitotriose and *N,N'*-diacetylchitobiose by *β-N*-acetylhexosaminidase has been developed and statistically evaluated. The method works with a borate-based background electrolyte that gives an electric charge to the neutral analytes and enables their separation. Using this method, the pH optimum, substrate specificity and further characteristics, have been investigated for the *β-N*-acetylhexosaminidase from*Aspergillus oryzae*. The work also reports on the development of an online enzyme assay. In this case, the mixing of substrate and enzyme, reaction and analytical separation occur directly in the capillary using so called "Transverse Diffusion of Laminar Flow Profiles" methodology. This approach offers a high degree of automation, enhanced repeatability and very low danger of sample loss or contamination.

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Keywords: *electrophoresis; enzymes; kinetics;*

P-0549

RP-HPLC AND CZE AS POWERFUL TOOLS FOR MONITORING OF REACTION INTERMEDIATES IN SYNTHESIS OF MAGNETIC RESONANCE CONTRAST AGENTS

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Magnetic resonance imaging (MRI) is one of the most powerful noninvasive methods in clinical diagnostics. To improve the contrast of the image, contrast agents are utilized. The contrast agents are often based on a transition metal or lathanide ion such as Gd^{3+}. In order to reduce their toxicity and prevent their accumulation in body tissues, the metal ions must be applied in form of highly stable complexes. For this purpose, the best ligands were found among cyclene (1,4,7,10-tetraazacyclododecane) derivatives containing carboxylate pendant arms.

In the development of new contrast agents, carboxyl groups are very often protected with *tert*-butyl ester groups. Among these derivatives, *t*Bu_3DO3A is of the highest importance. Therefore, reverse phase high performance liquid chromatography (RP-HPLC) and non-aqueous capillary zone electrophoresis (CZE) methods were evaluated for qualitative and quantitative analysis of *t*Bu_3DO3A, i.e. 1,4,7,10-tetraazacyclododecan-1,4,7-tris(*tert*-butylacetate) and two typical reaction by-products, i.e. *t*Bu_4DOTA (1,4,7,10-tetraazacyclododecan-1,4,7,10-tetrakis(*tert*-butylacetate) and *t*Bu_2DO2A (1,4,7,10-tetraazacyclododecan-1,4-is(*tert*-butylacetate). Both methods exhibited satisfactory efficiencies, good reproducibility and short analysis time. The optimized methods were successfully applied to monitoring of real reaction mixtures during synthesis of a new MRI contrast agent. No further sample pretreatment was necessary.

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Keywords: *Electrophoresis; Liquid chromatography; Imaging agents; Macrocyclic ligands;*

P-0550

STUDY OF THE ELECTROCHEMICAL REMOVAL OF CADMIUM FROM SIMULATED LEACHATE DILUTE SOLUTIONS

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In this work the electrodeposition of Cd from aqueous solutions with low concentration of the ion is studied, having in view the removal of this heavy metal via an electrochemical process. The metal was deposited on stainless steel electrodes. Deposits formed under different conditions were studied by linear and cyclic voltammetry techniques, X-ray powder diffraction, scanning electron microscopy and EDS surface analysis. Chronoamperometry was used to evaluate kinetic data of the deposition process. The effect of several ions concentration, pH and potential applied is evaluated in the electrodeposition efficiency. Model solutions prepared with multiple salts were tested in order to simulate an average composition of a leachate and to understand the influence of different electrolytes on the mechanism of electrodeposition. It was possible to recover electrodeposited Cd from solutions as dilute as 100 mg/l. The studies indicate that chloride, nitrate and sulfate have distinct influence on the voltammetric peak potential of electrodeposition and on the process. The studies also indicate the occurrence of simultaneous reducing processes that may be attributed to hydrogen evolution and nitrate reduction. Some morphological differences in the deposits may also be observed.

Keywords: *Cadmium; Electrochemistry; Kinetics; Environmental chemistry; X-ray diffraction;*

P-0551

ELECTROCHEMICAL BEHAVIOR OF RIFAMPIN DRUG AND ITS DETERMINATION INTHE PHARMACEUTICAL SAMPLES USING CARBON CERAMIC ELECTRODE

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In this work, the electrochemical behavior of RIF on carbon-ceramic electrode was investigateied by using cyclic voltametry at acetate-acetic acid buffer pH = 4. Sol-gel technology and using of silicated matrix that finally was crystallized as glassical crystals, was used for analytical investigation since former century. Sol-gel electrochemistry has provided extensive research range in analytical chemistry in last fifty years.

Sol-gel process was done on the base of hydrolysis and condensation of organometallic alkoxides following the gel formation process by forming polymeric bonds with M (OR)X.Carbon-ceramic electrode prepared in equeous solution contains rifampin has been used for investigation of electrochemical its behavior.Also, Electrocatalytic activities of proposed electrode were compared with other electrode substrates by cyclic voltammetry. Effective parameters such as solution pH, supporting electrolyte kind and its concentration, scan rate, applying frequency of square wave voltammetry, stirring speed and time of solution in the adsorption cell for RIF determination. RIF antibiotic adsorpted on carbon-ceramic electrode was determined by using cyclic voltammetry and square wave voltammetry and separation of adsorption cell from determination cell. Calibration curves was drawn for both methods and calculated detection limits 1.9 and 0.1 µM for cyclic voltammetry and square wave voltammetry, respectively. Calibration curves obtained from square wave voltammograms show two linear ranges from 0.010–0.168 µM and 0.49–56.6 µM.The CCE shows catalytic ability for the oxidation of RIF. The results show good stability for electrode and high sensivity in determination of low concentrations of RIF. Electrode efficiency as a voltammetric sensor was utilized for the determination of RIF in pharmaceutical samples involving 300 mg capsule and 150 mg/ml oral solution with satisfactory results.

Keywords: *Carbon ceramic electrode; Rifampin; Square wave voltammetry; Sol-gel; isoniazide;*

P-0552

EFFECT OF ALKALINITY AND THE NATURE OF THE BASIC SOLUTION ($CA(OH)_2$ AND $BA(OH)_2$) ON THE ELECTROKINETIC STABILITY AND RHEOLOGY OF THE DRILLING MUD

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The fall recurrently in alkalinity and pH of the drilling mud was observed during the use of local barite towards higher salt saturated mud for the drilling phase of 8" 1/2 of oil well at Hassi Messaoud in Algiers. This finding was confirmed on site oil, despite treatment with hydrated lime. This drop is due to alkalinity of the fine fraction of barite which tends to agglomerate easily. This results in the increase in rheological properties (the yield value and plastic viscosity) of mud during the drilling phase in question.

To overcome the difficulties associated with limitations in current understanding of such rheological behavior of the mud system studied, it is necessary to study the structure and stability of this system.

Drilling muds are dispersed colloidal systems, the dimensions and particle properties are important factors that determine the aggregative stability of disperse systems. Indeed, this stability is very sensitive to different factors governing the electrical phenomena and especially the physicochemical properties of the interfacial layer mineral solution. Among the physicochemical properties of this layer include: adsorption at the mineral interface, the orientation of the ions, the ionization of particles therein and the electrokinetic phenomenon appears. This can be a means to better understand the stability of suspensions.

For this purpose, this work aims to study the influence of the alkalinity of the mud and the nature of basic solution ($Ca(OH)_2$ and $Ba(OH)_2$) on the rheological parameters (plastic viscosity and yield value). And secondly, to give a microscopic approach to the stability of these parameters based on physical or chemical interactions existing between suspended particles, and the concept of zeta potential.

Keywords: *Zeta potentiel; Alkalinity; electrical double layer; drilling mud; barite;*

P-0553

OPTIMIZATION OF MERCURY COLD VAPOR GENERATION FOR ON-LINE ANALYSIS OF MERCURY SPECIES

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Mercury is one of the most dangerous elements in terms of its impact on the human body. Because the toxicity of mercury varies depending on its chemical species, it is very important to determine the exact amount of each species.

To determine the amount of each mercury species, speciation analysis is used. Speciation analysis combines a suitable separation method, such as gas or liquid chromatography with the appropriate detection method, such as inductively coupled plasma mass spectrometry (ICP-MS). Improved detection limits can be achieved using the mercury cold vapor generation (CVG) method. Cold vapor generation can be achieved using various compounds, but not all of them can be used in conjunction with high pressure liquid chromatography (HPLC) and ICP-MS detection.

In this work the mercury CVG method was optimized to determine the amount of mercury species using on-line HPLC-ICP-MS. We optimized the composition of the reagents required for CVG: the HCl concentration for the acidification of the effluent; the NaOH concentration for the stabilization of the $NaBH_4$ solution; the concentration of $NaBH_4$. In addition, the internal standard and flow rates were also optimized.

Our optimization resulted in reduced limits of detection (LOD) for methyl mercury species and inorganic mercury species. Methyl mercury LOD was reduced by almost a factor two to 0.021 ng/g and inorganic mercury by a factor of ten to 0.013 ng/g. There results suggest that our optimized method of CVG is useful for the speciation analysis of mercury in samples with low mercury content.

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Keywords: *Mercury; Liquid chromatography; Analytical Methods; Mass spectrometry; Trace analysis;*

P-0554

DETERMINATION OF BROMHEXINE ON CARBON PASTE ELECTRODE USING DIFFERENTIAL PULSE VOLTAMMETRY AND FIA WITH AMPEROMETRIC DETECTION

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Bromhexine is frequentlyused mucolytic agent and therefore, there is a demand for its fast and reliabledetermination. Thanks to its chemical structure, bromhexine is a suitablecandidate for electrochemical determination.

This fact was used for the development of new methods of determinationbased on differential pulse voltammetry (DPV) and flow injection analysis (FIA)with amperometric detection on glassy carbon paste electrode (GCPE) in a wall-jetarrangement. Optimum determination conditions of analysis were found. Incase of DPV, the optimum supporting electrolyteconsists of methanol and Britton-Robinson (B-R) buffer pH 9.0 (80:20, v/v). Theoptimum conditions for the FIA determination are: carrier solutionconsisting of methanol and ten times diluted B-R buffer pH 9.0 (80:20, v/v),detection potential +1.1 V, flow rate 1.5 mL min^{-1},the injected volume 100 µL, The possibility to increase sensitivity of DPV by preliminary adsorptionstep was tested with 5 min accumulation time, but significant decrease of detectionlimit was not obtained. The limit of detection for FIA was 0.9×10^{-8} mol $\text{L}^{-1}$and for DPV 5.8×10^{-7} mol L^{-1}. Applicability of the methods was tested by determination of realsamples of pharmaceutical preparations.

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Keywords: *Bromhexine; Glassy carbon paste electrode; Differential pulse voltammetry; Flow injection analysis; Amperometric detection;*

P-0555

HPLC/UV METHOD FOR DETERMINATION OF SELECTED BENZODIAZEPINES

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Introduction: Benzodiazepines are the most popular psychotropic drugs by doctors and drug addicts in the present. They are used mainly as sedatives, anxiolytics or as premedication before elective surgery due to its depressant effects on central nervous system. The side effects are mainly fatigue and sleepiness[1, 2]. The aim of this work was to developed HPLC/UV method for determination of six benzodiazepines (Alprazolam, Bromazepam, Clonazepam, Diazepam, Chlordiazepoxide and Oxazepam).

Experimental part: It was used ammonium acetate and formic acid for the preparation of mobile phase A. Acetonitrile was used as mobile phase B. Six powder standards of benzodiazepines, which were dissolved in methanol, was used further. The method was developed on the instrument Agilent 1200, which was equipped with a column Gemini 5µ C18 110A. The developed method was tested (its limits of detection (LOD) and quantification (LOQ), linearity, reproducibility, repeatability, precision and accuracy were determined).

Results: The developed method had following parameters: mobile phase A – 0.01M ammonium acetate + 0.1% (v/v) formic acid, mobile phase B – acetonitrile, total flow of mobile phase – 0,34 – 0,17 µl/min, mobile phase B gradient – 15 – 90% (0 – 17 min), column temperature – 20°C and spray – 20 µl. The parameters of method were following: LOD – 0,1 µl/min, LOQ – 0,2 µl/min, correlation linearity coefficients higher than 0,985, deviation of reproducibility and repeatability better than ±7% and deviation in precision and accuracy better than ±7%.

Conclusion: The obtained HPLC/UV method for determination of six benzodiazepines is suitable for introduction into practical usage in hospital laboratories.

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Keywords: *Liquid chromatography; Medicinal chemistry;*

P-0556

DIRECT VOLTAMMETRIC DETERMINATION OF ACIFLUORFEN, NITROFEN AND OXYFLUORFEN IN DRINKING AND RIVER WATER.

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The herbicides Acifluorfen, Nitrofen and Oxyfluorfen were developed for the protection of various crops against weeds. They are toxic to aquatic organisms, interfere with blood formation, and are endocrine disruptors. Many methods have been developed for their determination[1, 2]. Voltammetric techniques offer inexpensive, reliable and sensitive alternative to spectrometric determination of electroactive pollutants[3, 4]. This work is a continuation of our previous work on the same topic[3, 5]. This presentation is devoted to the determination of tested substances in model samples of drinking and river water, both alone and, if possible, in a mixture using a meniscus modified silver solid amalgam electrode (m-AgSAE). Acifluorfen was determined by DPV at m-AgSAE in 1 mL 1 mol?L^{-1} phosphoric acid and 9 mL of model sample of AF drinking/river water. Nitrofen and Oxyfluorfen were determined by DPV at m-AgSAE in a mixture of 1 mL 1 mol?L^{-1} NaOH, 3 mL of methanol and 6 mL of model sample of Nitrofen or Oxyfluorfen in drinking/river water. The calibration dependences were linear in the concentration range $1\cdot10^{-5}$ - $2\cdot10^{-7}$ mol·L^{-1} and the detection limit was around $2\cdot10^{-7}$ mol·L^{-1} in drinking and river water, respectively.

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Keywords: *Voltammetry; River water; Drinking Water; Herbicide; Determination;*

P-0557

DETERMINATION OF PATULIN IN COMMERCIAL BABY FOODS FROM TURKISH MARKETS BY HPLC

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Patulin is present globally in a wide range of fruit and vegetables. It has been identified in different types of fruits but was found more in apples, pears, peaches, and in their processed products like juices and puree[1, 2]. PAT is toxic for animals; it induces intestinal injuries, including epithelial cell degeneration, inflammation, ulceration; it has also been shown to be mutagenic, carcinogenic and teratogenic[3]. The EC Regulation 1881/2006 which indicates maximum levels for certain contaminants in food, sets the maximum limit of patulin equal to 10 μg/kg (or 10 μg/L) in baby food samples.

In this study, a fast, reliable, sensitive, and effective method with DAD detection for the quantitative analysis of PAT is described and evaluated according to the ICH guidelines. HMF was used as internal standard. These compounds are well separated on a Phenomenex Gemini C18 (110 A°, 250 x 4,6 x 3mm) column by using the mobile phase consisting of a mixture of acetonitrile (15:85; v/v, 15 mM CH_3COOH- pH=4.0) at a flow rate of 1.0 mL/min and 40 °C. Good sensitivity for all analytes was observed. The LOD and LOQ values were 5.02×10^{-4} mg L^{-1} and 1.52×10^{-3} mg L^{-1}, respectively.

In view of their wide use, both because they supply the nutritional needs for children, and because they consent easiness and rapidity in preparing meals, several samples of fruit-homogenized baby food were collected from Turkish markets to analyze and assess the patulin presence and their compliance with the limits provided by the law.

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Keywords: *Patulin; Baby Foods; Liquid Chromatography; Determination;*

P-0558

DETERMINATION PKA VALUES OF ANTIFUNGAL DRUGS BY UV SPECTROSCOPIC METHOD

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Dissociation constants (pK_a values) are useful physicochemical parameters describing the extent of ionization of functional groups with respect to pH. The knowledge of pK_a is important in drug discovery and development since the pharmacokinetic and pharmacodynamic properties of different protonation/ionization forms of the drug molecules may vary considerably [1].

In this study, the acidity constants of eight antifungal drugs (fenticonazole, isocanozole, itracanozole, ketocanozole, mikanozole, ornidazole, tinidazole, tiocanozole) have been determined in water and 10–20 % (v/v) MeCN-water mixtures at (25.0 ± 0.1) °C and in 0.1 mol L^{-1} KCl by UV spectroscopic method. Datas were processed using the program STAR (Stability Constants by Absorbance Readings) which calculates stability constants and molar absorptivities of the pure species by multi linear regression [2].

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Keywords: *Analytical methods; Antiviral agents; Drug design; Solvent effect; UV/Vis spectroscopy;*

P-0559

IMPORTANCE OF EVALUATING THE FALSE NON-COMPLIANCE AND FALSE COMPLIANCE IN THE DETERMINATION OF THE MINIMUM CONTENTS OF PROTEIN, DRY MATTER AND THE RATIO FAT DRY MATTER IN ZAMORANO CHEESE WHEN A NIR-PLS PROCEDURE IS USED

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Nowadays, near-infrared (NIR) spectroscopy means a useful methodology in process monitoring, determination of quality, geographical origin and adulteration of dairy products. However, because of the changes in spectra caused by various physical properties, a calibration against a reference method for the constituent of interest is required. Generally, a Partial Least Squares (PLS) regression is applied. The compliance of a maximum or a minimum limit for the quantity of a substance in food is mandatory in many of these determinations. So assessing the efficiency of NIR-PLS procedures in terms of detection capability (CDβ) evaluating the probabilities of false non-compliance (α) and false compliance (β) is needed.

This work was aimed to develop a rapid analytical tool for monitoring simultaneously the contents of fat, dry matter, protein and the ratio fat/dry matter in Zamorano cheese samples by NIR spectroscopy. Zamorano cheese is protected with a Designation of Origin and registered as Protected Designation of Origin, which represent the system of recognition of a distinctive quality within the European framework. Calibration models based on a PLS regression of the percentage in weight of every constituent on the spectra recorded were estimated. Therefore, values of the explained variance of the response between 92.54 and 96.57% were obtained, and the mean and the standard deviation of the absolute value of the relative error in calibration ranged from 0.66 to 1.05% and from 0.43 to 0.87%, respectively. The trueness of every method was also ensured, and the minimum contents of protein, dry matter and the ratio fat/dry matter according to specific regulations were calculated.

Experimental values of CDβ equal to 24.57% for protein, 53.28% for dry matter and 43.78% for the ratio fat/dry matter were obtained ($\alpha = \beta = 0.05$)

Acknowledgements: *financial support through projects CTQ2011-26022 and BU108A11-2. M.L. Oca thanks to University of Burgos for her FPI grant.*

Keywords: *NIR; Partial Least Squares; Cheese; False compliance; Capability of detection;*

P-0560

INVESTIGATION OF SODIUM BOROHYDRIDE ELECTROOXIDATION MECHANISM ON SILVER ELECTRODE IN BASIC MEDIUM

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As fossil fuel sources come to an end and problems due to pollution rises, fuel cells with environment friendly reagents (like hydrogen) become more important. Hydrogen is one of the preferred energy sources, which can be hard to store due to limited area capacity and exploding hazards. At this point a suitable energy carrier compound, sodium borohydride ($NaBH_4$), steps in and conducts in-situ hydrogen generation through hydrolysis reaction within its superior characteristics such as non-flammability, stability and recyclability.

In this study, the electrochemical oxidation mechanism of $NaBH_4$ on silver electrode in sodium hydroxide support electrolyte was investigated. The effect of sodium hydroxide concentration and optimum conditions to obtain maximum oxidation in presence of oxidative reagent like potassium permanganate were also investigated.

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P-0561

EXPERIMENTAL AND COMPUTATIONAL STUDIES ON THE THERMAL DECOMPOSITION OF NITROAZIDOBENZENES

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In this combined experimental and theoretical study the thermal decomposition of 2-nitroazidobenzene (**I**), 2,4-dinitroazidobenzene (**II**) and 2,4,6-trinitroazidobenzene (**III**) to yield benzofuroxan (**IV**), 4-nitrobenzofuroxan (**V**) and 4,6-dinitrobenzofuroxan (**VI**) were investigated by thermoanalytical (TG, DSC) and computational methods. Interestingly, furoxan formation was not observed for 4-nitroazidobenzene (**VII**) under heating due to the *para* position of the nitro group in the benzene ring. All compounds were characterized by elemental analysis, vibrational (IR) spectroscopy and mass spectrometry. The crystal structure of compound **III** was determined by single crystal X-ray diffraction [1a, b]. All calculations were carried out using the Gaussian G09W (revision B.01 [2a]. DFT-based structure optimizations and frequency analyses were performed at the B3LYP/cc-pVDZ level of theory [2b]. The structural parameters of the fully optimized compound **III** was in good agreement with the single-crystal X-ray data. The enthalpies of formation for compounds **I**, **II**, **III**, **IV**, **V** and **VI** were calculated using the complete basis set (CBS-4M) method of Petersson and coworkers in order to obtain accurate energy values [2c]. The enthalpies of decomposition for compounds **I**, **II**and **III** were obtained from calculated enthalpies of formation according to Hess Law and were compared with the experimental values which were available from DSC analysis and were also found to be in very good agreement.

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Keywords: *Thermal Decomposition; CBS-4M; Nitroazidobenzene; IR; TG;*

P-0562

NITROMETHANE ELECTROCHEMICAL SENSING METHOD FOR AN EXPLOSIVE TRACE DETECTOR BY CONCENTRATION IN LIQUID MEDIA

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During the past ten years, the terrorism menace has increased and the development of efficient explosive detection devices has become an urgent worldwide necessity. In this context, the CEA (Commissariat l'Energie Atomique et aux Energies Alternatives) started several projects aimed at developing detectors of explosives traces. Nebulex is a patented device which solubilises vapors or particles of explosive (or precursor) in a tank via a spray formation. The solubilised molecules can be detected in-situ using an adapted reagent to a technique of detection. First, colorimetric and fluorescent methods were used in associate with specific reagents developed for peroxides detection. In this study, we evaluated electrochemistry as a new method for the detection of a nitro compound, the nitromethane.

Whereas aromatic nitro compounds such as trinitrotoluene (TNT) have already been widely studied, nitromethane doesn't seem to have attracted much interest. Nitromethane is a constituent of artisanal explosive compositions, and like the other nitro compounds, it can be detected by the electrochemical reduction of the NO_2 group. The objective of this study is to define and optimize conditions for the detection with a simple and robust system of electrodes.

The higher intensity of reduction was obtained in neutral media and by using a gold electrode with a simple system. In these conditions, a limit of detection (LOD) of 3 µmol/L of nitromethane was achieved in the absence of dissolved oxygen. In air environment, which is more representative of real condition encountered with Nebulex device, the LOD grows to 12 µmol/L due to increase of noise.

An important constraint imposed by the project is to minimize the system for a portable application in the Nebulex device. For this, a portable potentiostat and a screen-printed electrodes system were evaluated and compared with laboratory equipment.

Keywords: *electrochemistry; sensors; trace analysis;*

P-0563

MASS SPECTROMETRIC APPROACH TO EVALUATION OF HISTORICAL PAINTINGS BY IDENTIFICATION OF PRUSSIAN BLUE AND INDIGO

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Prussian blue and indigo are very famous and widely used blue pigments. They often exhibit similar properties in paintings and they are highly insoluble in water and common organic solvents. Prussian blue is the synthetic pigment discovered at the beginning of the 18th century in Berlin, natural indigo was produced from plant material since ancient times and used up to the end of the 19th century when it was replaced by the synthetic dye.

The aim of this work was to develop a fast and sensitive method for analysis of both pigments of high historical importance.

The experiments were performed using a Q-TOF Premier mass spectrometer (Waters, Manchester, UK) by flow injection analysis with negative electrospray ionization. The compounds were subsequently detected after simple sample preparation based on two chemical reactions in alkaline solution: decomposition of Prussian blue and reduction of indigo with dithionite to soluble leucoindigo.

The main advantage of the developed procedure is that no chromatographic separation is required. The proposed method is fast (2 minutes runtime), very sensitive (LODs for Prussian blue and indigo are 47 pg and 59 pg in injection, respectively) and has a wide dynamic range (linear calibration was observed from 10 to 5000 ng/mL, injection volume 5µL).

The method was successfully applied for identification of Prussian blue in samples taken from the painting of 'Crucifixion', St. Sebestian church on St. Hill in Mikulov, Czech Republic, and results were confirmed by Raman spectroscopy. This technique can be used for fast screening of two blue pigments in small samples of historical and art objects.

Acknowledgement: *The support by the Ministry of Education, Youth and Sports of the Czech Republic (ME10013), Operational Program Research and Development for Innovations - European Regional Development Fund (project CZ.1.05/2.1.00/03.0058) and by Palacky University (PrF_2012_020) is gratefully acknowledged.*

Keywords: *Mass spectrometry; Dyes/Pigments;*

P-0564

POTENTIOMETRIC DETERMINATION OF PIROXICAM IN PURE AND PHARMACEUTICAL DOSAGE FORMS

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Different analytical methods for determination of piroxicam (PX) in various real samples were summarized in [1]. However, some new methods based on relatively simple and inexpensive equipment were desirable. Regarding that, the method based on employing the analyte pulse perturbation technique to the Bray-Liebhafsky (BL) oscillatory reaction as very nonlinear system, as well as using the potentiometric monitoring of analyte perturbation, promise the alternative to some instrumental methods due to its low cost instrumentation and relatively rapid detection procedure.

For quantitative determination of PX [2], the BL matrix in a stable non-equilibrium stationary state that was generated in continuously fed well stirred tank reactor, was used. The BL matrix response to perturbations by different concentrations of PX is followed by a Pt electrode. The method relies on the linear relationship between maximal potential shift, ΔE_m, and the added PX concentration in the range of 6.8×10^{-5}–1.9×10^{-3} mol L^{-1}. Under the optimized conditions (T = 64.0°C, $[H_2SO_4]_0 = 8.55\times10^{-2}$ mol L^{-1}, $[KIO_3]_0 = 5.90\times 10^{-2}$ mol L^{-1}, $[H_2O_2]_0 = 1.50 \times10^{-1}$ mol L^{-1} and $j_0 = 2.95\times10^{-2}$ min^{-1}), the regression equation of the standard series calibration curve is $\Delta E_m = -5.9 - 14671.9 \times c_{PX}$. The method has a rather good sample throughput of 30 samples h^{-1} with the limit of detection LOD = 6.3×10^{-5} mol L^{-1}, precision RSD = 4.2 %, as well as recoveries RCV ≤ 104.7 %. Applicatibility of the proposed method to the direct determination of PX in different pharmaceutical formulations (tablets, ampoules and gel) was demonstrated.

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Keywords: *piroxicam; potentiometric; oscillatory reaction;*

P-0565

DETERMINATION OF DIFFUSION COEFFICIENTS BY TAYLOR DISPERSION ANALYSIS USING CAPILLARY ELECTROPHORESIS INSTRUMENTATION WITH VARIOUS DETECTORS

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Determination of diffusion coefficient represents an important task for many branches of the research ranging from pure physical chemistry to medicine where the diffusion of pharmaceutical active substances has an impact on the physiologic state of organism. There a plenty of methods used for such measurements. A special place is hold by capillary electrophoresis (CE). CE represents a fast, low cost, easy operation technique that needs only a few microliters of samples. On the basis of the Taylor and Aris theory, CE can be utilized for the measurements of the rate of the diffusion during the flow of compounds through the capillary. The aim of our work was to apply this methodology, called Taylor dispersion analysis (TDA), for measurements of the diffusion coefficient of model compounds employing various detectors that have an additional power (e.g. can be applied for UV non-absorbing compounds, provides structural information). In our study, three types of detectors were used: (**i**) contactless conductivity detector for analysis of some saccharides, (**ii**) laser-induced fluorescence detector for analysis of carbogenic quantum dots, and (**iii**) single quadrupole mass spectrometer for analysis of a mixture of aminoacids. We observed that the utilization of such detectors can be very profitable for the determination of diffusion coefficients.

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Keywords: *diffusion coefficient; capillary electrophoresis;*

P-0566

THE PROTOELECTRIC POTENTIAL MAP (PPM).A UNIFORM ENERGY SCALE OF THE CHEMICAL POTENTIAL OF THE PROTON AND ELECTRON IN DIFFERENT MEDIA

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We recently introduced a unified *Bronsted acidity* scale on the basis of the chemical potential of the proton in any medium allowing the comparison of pH values of different media. We defined the reference state of maximum acidity as the standard chemical potential of the proton in the gas phase (ideal H^+ gas, 1 bar, 298.15 K), arbitrarily set to 0 kJ mol^{-1}. The acidity and hence the chemical potential of the gaseous proton is lowered by the interaction with any type of a medium i.e. complexation of H^+ in the gas phase, solution, or in the solid state. [1]

The definition and determination of absolute standard reduction potentials is under discussion since a long time. From a theoretical point of view as well as for many applications reduction potentials comparable between different solvents are of great interest and may lead to completely new insights and applications. [2] We define the absolute reduction potential scale totally analogous to the absolute pH scale setting the chemical potential of the electron in the gas phase (ideal e^- gas, 1 bar, 298.15 K) to 0 kJ mol^{-1}.

The Hydrogen Evolution Reaction (HER) correlates the pH scale with the redox scale. Our intention is to establish a novel uniform scale for the chemical potential of the proton as well as for the electron leading to the Protoelectric Potential Map (PPM). Once a suitable absolute redox scale pe_{abs} is adopted the PPM as a 2D plot of pe_{abs} versus pH_{abs} allows one to determine the optimal solvent for a given redox reaction. The Poster will present our recent ongoing efforts to establish the PPM in liquid media with the help of electrochemical measurements and supported by quantum chemical thermodynamic calculations. [3]

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3. In preparation.

P-0567

KINETIC SPECTROPHOTOMETRIC DETERMINATION OF N-ACETYL-L-CYSTEINE BASED ON THE REDUCTION OF COPPER(II)-NEOCUPROINE REAGENT

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Novel simple kinetic spectrophotometric method for the determination of *N*-acetyl-L-cysteine (NAC) has been developed and validated. NAC is a synthetic aminothiol antioxidant that has been in clinical use for more than 40 years, primarily as a mucolytic agent and in the management of paracetamol (acetaminophen) poisoning.

The proposed method is based on the reduction of Cu(II)-neocuproine reagent to Cu(I)-neocuproine with the analyte, in a Britton-Robinson buffer solution (Acetic/Boric/Phosphoric acid buffer solution, pH = 3.0). The non-stable absorbance of the formed Cu(I)-neocuproine chelate is measured at 458 nm.

The proposed redox reaction is very fast, but the coloured product of the reaction is unstable probably due to oxidation with the oxygen from the air. Therefore is very important to measure the signal in kinetic part of the reaction (under dynamic conditions in which the concentrations of reactants and products are changing as a function of time).

The initial rate and fixed time (at 1 min) methods were utilized for constructing the calibration graphs. Initial reaction rates were determined from the slopes of the absorbance-time curves. The logarithms of the reaction rates were plotted as a function of logarithms of NAC concentrations. The graph was linear in concentration range from 6.0×10^{-7} to 8.0×10^{-5} mol L^{-1} with the regression equation $y = 1.0181\,x + 2.9927$ ($R^2 = 0.9998$). The slope of the calibration curve (1.0181) confirmed the first order reaction.

The graph of the fixed time method was linear in concentration range from 6.0×10^{-7} to 8.0×10^{-5} mol L^{-1} with the regression equation $y = 7111\,x - 0.0027$ ($R^2 = 0.9999$), and the limit of detection 1.7×10^{-7} mol L^{-1}.

The proposed methods were successfully applied for the determination of NAC in its commercial pharmaceutical formulations and compared to the official iodimetric method.

Keywords: *kinetics; analytical methods; UV/vis spectroscopy; reduction; redox chemistry;*

P-0568

DETECTION AND QUANTIFICATION OF DICLOFENAC IN WATER

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Nonsteroidal anti-inflammatory drugs such as diclofenac are one of the most widely used drugs in human and veterinary medicine at present. Because the rate of elimination of diclofenac in communal sewage treatment plants is low[1], diclofenac is ubiquitously present in the aquatic environment. Although, diclofenac was not found in surface waters at concentrations that were high enough to cause acute toxic effects[2], its presence can lead to long-term effects due to bioaccumulation or additive and synergistic effects by mixing it with different pharmaceutically active compounds.

To protect both the environment and human health, it is vital to develop reliable tools for detecting and monitoring diclofenac in water. The most common analytical techniques used to determine pharmacologically active substances in water at present are gas or liquid chromatography combined with mass spectrometry[3, 4]. Those methods are very sensitive, but have the disadvantage of requiring sample preparation and cleanup.

Optical biosensors fulfill the requirements to be sensitive, simple, cost-effective and quick to perform. Furthermore they do not require extensive sample preparation.

In this work Reflectometric Interference Spectroscopy (RIfS)[5] has been used as optical detection method to detect and quantify diclofenac in water samples. RIfS is a label-free and time resolved method, also ideal for optimizing surface chemistry, understanding matrix effects and calibrating the sensor.

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Keywords: *biosensors; immunoassays;*

P-0569

VOLTAMMETRIC DETERMINATION OF METRONIDAZOLE BY MEANS OF A MERCURY MENISCUS MODIFIED SILVER SOLID AMALGAM ELECTRODE

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Metronidazole (2-(2-methyl-5-nitro-1*H*-imidazol-1-yl)ethanol) belongs to the group of antibiotics, amebicids and antiprotozoal medicaments, and it is known as a cancerogenic compound. This contribution is focused on the determination of metronidazole using modern voltammetric techniques, namely direct current voltammetry (DCV) and differential pulse voltammetry (DPV) at a mercury meniscus modified silver solid amalgam electrode (m-AgSAE), in drinking and river water model samples and on the determination of its content in selected pharmaceutical formulations. The main advantages of m-AgSAE are: Its wide potential window in cathodic region (cca 1,8 V span), easily renewable surface of the electrode and also non-toxicity as compared to mercury electrodes. It was confirmed in this work that it is possible to determine metronidazole in the concentration range of 0.2 to 100 μmol.l^{-1} in the medium of Britton–Robinson buffer of pH 8.0 with the limit of quantification (*LOQ*) 0.32 μmol.l-^{1} and 0.19 μmol.l^{-1}reached using DCV and DPV, respectively. Moreover, the practical applicability of the newly developed methods was verified upon the direct determination of metronidazole in model samples of drinking and river water in the concentration range of 0.2 to 10 μmol.l^{-1} with $LOQ \approx 0.2$ μmol.l^{-1} (for all the applications tested). The contents of metronidazole in pharmaceutical formulations Efloran® (Krka) and Entizol® (Polpharma) was successfully determined by the standard addition method and by the calibration curve method using both voltammetric methods developed.

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Keywords: *Electrochemistry; Analytical chemistry; Voltammetry; Amalgams;*

P-0570

PHOTOCHEMICAL VOLATILE FORMS GENERATION FOR DETERMINATION OF SELENIUM BY QUARTZ FURNACE ATOMIC ABSORPTION SPECTROMETRY

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This work is focused on the determination of selenium in aqueous samples using photochemical generation of its volatile forms coupled with atomic absorption spectrometry. This emerging approach of sample introduction is a useful alternative to conventional chemical and electrochemical generation due to its simplicity, versatility and cost effectiveness. Method is based on the fact, that in the presence of a low molecular weight organic acid (formic, acetic, propionic or malonic), inorganic selenium(IV) is converted by the effect of UV radiation into volatile species (selenium hydride, selenium carbonyl, dimethyl selenide, diethyl selenide, respectively). In this approach of sample introduction, a flow-through photoreactor consisting of PTFE tubing (1.0 i.d. / 2.0 o.d.) wrapped around the low-pressure Hg vapor UV lamp was first constructed. Optimum experimental conditions for photochemical vapor generation using formic or acetic acid were then found. Attention was paid to optimize the carrier gas flow rate as well as the auxiliary hydrogen flow required for complete atomization of generated volatile selenium form in externally heated quartz furnace. Further key parameters were also optimized: effects of additives and acid concentration or the time of irradiation of the analyte (it depends on the length of PTFE tubing and sample flow rate). A detection limit of 1.0 μg L^{-1} Se(IV) with a repeatability of 3.4 % (RSD, n = 10, formic acid) was obtained using this coupled technique. Consequently, the generation efficiency was investigated. Except of classical methods (comparing of slope of calibration curves of photochemical and reference chemical generation; determination of residual analyte in waste), radiotracer ^{75}Se was used. Similarly, interference study and verification of proposed method on real samples were realized.

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Keywords: *UV photochemical generation; volatile form; atomic absorption spectrometry; selenium;*

P-0571

STUDY OF COLUMNS MACROCAPILLARY THICK FILM IN GAS CHROMATOGRAPHY: EFFICIENY AND CAPACITY OF INJECTION

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As part of a study columns macrocapillary a film thick and grafted in gas chromatography, recently developed as a friendly columns, we calculate an efficiency criterion impregnation has adapted the kinetic of these columns.

However we show that for this, it does not involve the resistance to the transfer of liquid matter, considered negligible usual columns with a thin film. We must also take into account the interfacial resistance, expected by the theory of Khan and not by the equations of classical GOLAY. This work contributes to end a controversy thirty years old on a life of the term interfacial resistance.

However we show that it is possible to preserve the full effectiveness of these columns within easy injection of the kind of columns, except for the rigor of solutes apolar, priced at a high dilution in the solvent. But these injections are perfectly possible if consent is a significant loss of efficiency, thanks to a high dilution and at a rate well above the optimum. It remains then these columns substantial benefits compared to packed columns.

Keywords: *Gas chromatography; Macrocapillary columns; Thick Film; Efficiency of impregnation; Quantity injection;*

P-0572

DEVELOPMENT OF RP-HPLC METHOD FOR VINCRISTINE SULFATE, DAUNORUBICIN AND DOXORUBICIN

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Daunorubicin (DAU) and doxorubicin (DOX) are the most commonly used anthracycline anticancer antibiotics. Their molecules consist of a tetracyclic quinoid aglycone and an amino sugar–daunosamine, which are linked by a glycoside bond [1]. Vincristine sulfate (VCR) is a natural vinca alkaloid derived from the periwinkel plant *Catharantus roseus G. Don*. It has been used in variety of human neoplatic disorders for nearly 40 years.

In this study, simple, reliable, and rapid RP-HPLC method has been developed for the determination of these drugs and this method has been succesfully applied human urine samples. These compounds are well separated on a C18 column by using the mobile phase consist of a mixture of acetonitrile (50:50; v/v, 20 mM H_3PO_4- pH = 9.5) at a flow rate of 1.5 mL/min. Good sensitivity for all analytes was observed with DAD detection.

For each compound, the calibration curves were linear over a concentration range of 1–12 µg.mL^{-1}. Limits of detection (LOD) and the limits of quantification (LOQ) were found for VCR 0.2145 and 0.6542 µg.mL^{-1}; for DAU 0.045 and 0.1226 µg.mL^{-1}; for DOX 0.0901 and 0.2731 µg.mL^{-1}.

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Sparreboom, *Anal. Biochem.* **1999**, *266*, 216–221.

Keywords: *Analytical Methods; Liquid chromatography; Cancer; Drug delivery; Acidity;*

P-0573

RAPID DETECTION OF ESCHERICHIA COLI USING MICROANALYZER BASED ON THE PRESENCE OF O-NITROPHENOL

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With persistent occurrence of water- and food-borne diseases outbreaks such as those caused by pathogenic *Escherichia coli*, there is an urgent need for a (bio) analytical sensor that can rapidly detect and identify the source of contamination in a timely manner. Standard methods usually involve culturing which needs at least 18 h. In this work, an analytical method for rapid detection of *E. coli* in water sample was developed. *E. coli* was incubated in a lactose-rich nutrient containing Ortho-Nitrophenyl-β-galactoside (ONPG) substrate to induce the activity of β-galactosidase enzyme in *E. coli*. In a controlled environment, β-galactosidase enzyme can break β-galactoside bond in lactose, releasing *o*-nitrophenol. To allow the accumulation of the *o*-nitrophenol in the sample vials, the bacteria were incubated under anaerobic condition. To investigate the minimum period required for the production of the *o*-nitrophenol, the bacteria were incubated in different sample vials under different incubation periods. The incubation periods were varied from 0 to 4 h with 30 min intervals. To detect the *o*-nitrophenol, headspace analysis of *o*-nitrophenol were done using microAnalyzer, a miniaturized gas chromatography – differential mobility spectrometry (GC-DMS) system. It was found that the *o*-nitrophenol was able to be detected by microAnalyzer within 200 s. It was also found that the minimum incubation period was 2.5 h, whereas the optimum incubation period was 3 h. To our knowledge, our method offers the most rapid incubation and detection of *E. coli* and the first application of microAnalyzer in this field. With the microAnalyzer being portable, could be operated using ambient air, does not need oven, and has a low-energy requirement, to mention few, this method is very attractive to be applied for an on-site detection of *E. coli,* providing a better approach in the *E. coli* outbreak risk management.

Keywords: *Escherichia coli; microAnalyzer; microbial water quality monitoring;*

P-0574

DYNAMIC EXTRACTION OF OIL PRODUCTS FROM CONTAMINATED SOILS

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Control of oil content in contaminated soils is a very actual task because of increasing development of oil industry. Existing methods used for the determination of oil hydrocarbons in soils are routine and time-consuming due to the necessity of laborious sample pretreatment prior to instrumentation analysis. Hence, the development of new methods for organic analysis of soils is required.

The use of flow-through extraction systems (FTES) for dynamic extraction of hydrocarbons from soils is very promising. Microcolumns (MC) packed with a particulate sample are well-know FTES[1]. In the present work cylindrical MC were applied to the analysis of spiked with oil hydrocarbons (OH) and contaminated soil samples. Tetrachlormethane was used as solvent for MC extraction of OH prior to the detection by IR-spectrometry. The dependence of extraction efficiency on soil type, eluent volume and extraction time was systematically studied. Elution curves show that the eluent volume of 20–30 mL is enough for extraction in MC. Results on OH content obtained using extraction in MC, Soxhlet extraction and batch extraction were comprared. It has been showm that the recovery of OH after extraction using MC is 70–94%. No filtration step is required before the determination of OH in the MC effluent. The technique enables the extraction to be performed within 20–30 minutes only.The proposed approach to the sample pretreatment in organic soil analysis opens a new door into the development of new analytical methods for the control of oil contaminated soils.

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Keywords: *extraction; oil products; soil;*

P-0575

THE INVESTIGATION OF THERMAL DECOMPOSITION OF NITRO-CHLORO-AZIDOBENZENES WITH THERMOANALYTICAL AND COMPUTATIONAL METHODS

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1,2-dichlorobenzene and 1,2,3-trichlorobenzene were nitrated with HNO_3/H_2SO_4. The obtained mixtures were converged into azido-chloro-nitrobenzenes via nucleophilic subtitution reaction with NaN_3 as described in the literature[1]. The components in the precipitate were seperated by fractional crystallization and were investigated by TG. Benzofuroxan formation after elimination of N_2 at 100–120 °C was observed from IR, MS, and XRD results in case of nitro and azide groups are next to each other in the aromatic ring (Fig.1). Additionally, the released energies for exothermic reaction of *o*-nitroazidobenzenes were measured by DSC. On the other hand an obvious detonation reaction was observed for dinitrodiazidobenzenes at 130–150 °C.

All theoretical calculations were carried out using the Gaussian G09W (revision B.01) program package.[2] DFT-based structure optimizations and frequency analyses were performed at the B3LYP/cc-pVDZ level of theory.[3] The enthalpies of formation of both reactants and products were calculated using complete basis set (CBS-4M) method of Petersson and coworkers in order to obtain accurate energies.[4] From the calculated heat of formations the enthalpies of decomposition were calculated according to Hess's Law and were compared with the experimental values which were available from DSC analysis. The good agreement between the experimentally observed enthalpies of decomposition and the CBS-4M calculated values gives credence to the accuracy of the applied CBS-4M method.

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Keywords: *Benzofuroxan; CBS-4M; DFT; Nitroazidobenzene; Thermal analysis;*

P-0576

AN ULTRASENSITIVE BIOSENSOR FOR C-ERBB-3 DETECTION BASED ON ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

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Breast cancer is one of the most common cancers in women. Becouse of the aggresive behaviour, and can be diagnosed early, breast cancer is one of the most cancer type that is studied in the relation between diagnostic and treatment methods.[1, 2]

The c-erB3 gene, which takes part on chromosome 12q13 and codes for glycoprotein and is 180 000 molecular weight, is a declared member of the type I family of growth factor receptors.[3] C-erB3 protein is attended in normal human fatal and adult tissues[4], and also known as expressed at protein levels and mRNA in tumor cells and primary tumor material[4, 5].

An electrochemical bio-sensor system based on electrochemical impedance spectroscopy is developed to detect c-erB3 by anti-c-erB3. AntiCerB was immobilized through covalent coupling with cysteamine which formed a self-assembled monolayer on gold electrodes covered with heksenditiol and AuNP. Electrochemical impedance spectroscopy(EIS) and cyclic voltammetry (CV) techniques were used to detect c-erB3 and to characterize the immobilization process. Kramers–Kronig Transform was performed on the experimental impedance data. To provide the biosensor's currency, experimental parameters were optimized. The obtained results provided a linear response range from 0,2 pg to 1,4 pg c-erB3.

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Keywords: *Breast cancer; biomarker c-erbB-3; biosensor; Electrochemical impedance spectroscopy;*

P-0577

A NOVEL, ULTRA SENSIBLE BIOSENSOR BUILT BY LAYER-BY-LAYER COVALENT ATTACHMENT OF A RECEPTOR FOR DIAGNOSIS OF TUMOR GROWTH

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In the presented research, a novel, ultra sensible biosensor for the impedimetric detection of vascular endothelial growth factor (VEGF) is introduced. The human vascular endothelial growth factor receptor 1 (VEGFR1, Flt-1) was used as a biorecognition element for the first time in the literature. The immobilization of VEGF-R1 on glassy carbon electrodes was carried out by layer-by-layer covalent attachment of VEGF-R1. The electrochemical properties of the layers constructed on the electrodes were characterized by electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV). The differences in electron transfer resistance (R_{et}) between the working solution and the biosensor surface, recorded by the redox probe $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$, confirmed the binding of VEGF to VEGF-R1. The new biosensor allowed a detection limit of 100 fg/mL with a linear range of 100 fg/mL to 600 fg/mL to be obtained. The biosensor also exhibited good repeatability (with a correlation coefficient of 1.95 %) and reproducibility.

Keywords: *Tumor growth; Vegf; Vegf-R1; Biosensor; Electrochemical impedance spectroscopy;*

P-0578

COMPARISON OF DIRECT INFUSION MASS SPECTROMETRY, HPLC/MS AND ION MOBILITY/MS IN ANALYSIS OF POLYACRYLIC ACIDS

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Polyacrylic acids (PAA) belong to potential environmental pollutants due to their extensive use and solubility in water contributing to their distribution in environment.

The direct infusion and chromatographic experiments were performed using an LCQ DUO ion trap mass spectrometer equipped with electrospray ion source (Thermo Finnigan, San Jose, USA) and an HPLC Agilent 1100 Series chromatograph (Agilent, USA) with Gemini column (5μm C18, 110 A; Phenomenex, Torrance, USA). Ion mobility mass spectrometric experiments were carried out using a SYNAPT G2-S spectrometer (Waters, Manchester, UK) by flow injection analysis with negative electrospray ionization.

Direct infusion mass spectrometry using electrospray ionization in negative ion mode allowed fast detection of several oligomeric series, but the detail polymer characterization required time consuming inspection and interpretation of spectra.

Chromatographic separation (LC/MS) is more time-consuming but allowed obvious differentiation of oligomeric series with different end groups. Subsequent LC/MS/MS analysis contributed to the identification of the end group.

Ion mobility mass spectrometric experiments were used to provide further structural information by separation of the individual charge series. It allowed fast characterization of PAA samples and drift time vs *m/z* plots can be used as fingerprints for the differentiation of samples. It is evident that some separation (ion mobility or chromatographic) is very useful for complicated PAA mixture analysis. Hyphenation of chromatography, ion mobility and mass spectrometry can offer a very useful tool for PAA analysis. Evaluation of orthogonality of chromatographic and ion mobility is under study.

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Keywords: *Mass spectrometry; Liquid chromatography; Polymers;*

P-0579

SUBSTITUTION OF WATER BY METHANOL IN AQUEOUS NORMAL PHASE LIQUID CHROMATOGRAPHY

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The effects of mobile phase composition on the separation of phenolic acids on four types of hydrosilated silica columns (hydrosilated silica, diamond hydride, cholesterol and bidentate column) in acetonitrile/water and acetonitrile/methanol mobile phases, both in the ANP and RP modes in the full mobile phase composition range including both aqueous normal phase (ANP) and reversed-phase (RP) HPLC modes were investigated. In case of ANP, the analyte is distributed between a water rich stationary layer and the bulk mobile phase with a lower water concentartions, probably by a combination of partition and adsorption mechanisms. Phenolic acids elute in the order of increasing polarities i.e. with increasing number of polar groups (OH, -COOH, etc.) opposite to the reversed-phase mechanism.

The typical mobile phase for ANP chromatography includes acetonitrile containing 1-15% of buffered or acidified water. We have found that methanol in buffered mobile phase can substitute water in the ANP mode. In both types of mobile phases, the elution order of selected phenolic acids in the ANP mode is identical and their retention decreases as the concentration of water or methanol in mobile phase increases. Phenolic acids are more strongly retained in ACN/methanol on hydrosilated silica column in comparison to their retention on the same column in ACN/water mobile phase, whereas the retention of phenolic acids on cholesterol and diamond column is slightly higher in ACN/water than in ACN/MeOH. The retention of phenolic acids on bidentate column is comparable in both mobile phases. Slightly impaired resolution and selectivity was observed in ACN/MeOH as the mobile phase in comparison to the ACN/water on all columns tested.

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Keywords: *aqueous normal phase LC; phenolic acids; silica hydride material;*

P-0580

EXPERIMENTAL DESIGN APPLIED ON PYROHYDROLYTIC EXTRACTION OF FLUORINE AND CHLORINE FROM COAL

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This research has been focused on the determination of fluorine and chlorine content in the lignite coal by applying a experimental design approach. A pyrohydrolysis (Phy) apparatus system was constructed, and the pyrohydrolytic parameters were evaluated and optimized by two statistical methods: Plackett-Burman (PB) design and response surface methodology (RSM). Halogen content in the absorption solution was measured by ion selective electrode (ISE) and by ion chromatography (IC).

Results of PB designed experiments indicated that the most important parameters on Phy-ISE determination of fluorine in coal were time, temperature and oxidation atmosphere, while the Phy-IC determination of chlorine was strongly influenced by absorption solution and temperature. These screening experiments signified that during the pyrohydroytic extraction and within the range of investigated parameters, in some degree the chlorine in coal could volatilizied as molecular chlorine.

The RSM is a statistical modeling technique employed for multiple regression analysis using the data obtained from designed experiments. The statistical models applied were suitable for predicting and optimizing of fluorine determination within the range of variables used.

It was concluded that optimal conditions for Phy-ISE determination of fluorine in coal were: 0.25 g of coal sample, 0.30 mL min^{-1} of oxygen flux, a temperature of 1100 °C, 15 min of pyrohydrolysis and Na_2CO_3 (2 mmol L^{-1}) as adsorption solution. The limit of detection of the proposed method was 20 μg g^{-1}, with good recovery (95 %) and relative standard deviation value less than 5 %. According to the applied experimental design, the pyrohydrolytic extraction was unsuitable for chlorine in coal determination.

P-0581

EFFECTS OF LIQUID MANURE AMENDMENT ON ACCUMULATION OF HEAVY METALS IN WHEAT AND BARLEY

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An experiment was carried out to evaluate uptake of heavy metals by wheat and barley in the presence of liquid manure amendment. Wheat and barley seedlings were grown on a filter paper in a 12-cm diameter Petri dish. Additionally, wheat seedlings were grown in pots containing unpolluted agricultural soil. All the seedlings were irrigated three times per week with prepared solutions: first solution with composition similar to rain water, second solution containing Cd, Cu, Zn, Pb, Ni, Fe, Mn, Hg and As, and the third solution of liquid manure containing the same heavy metals as the second one. After 10 days the plants were weighed and 1 g of plant tissue was prepared for ICP-OES analysis by microwave digestion with mixture of HNO_3 and H_2O_2. The results have shown that the uptake of arsenic and mercury was highest for both plants grown in Petri dish. Beside high arsenic content, the pot grown wheat contained a high amounts of iron and manganese, probably due to the adsorption of nickel, cadmium, cooper and mercury on soil phases. On the other hand, the wheat grown without soil had higher content of nickel, cadmium and cooper, while the uptake of manganese and iron was lowered. The lower uptake of all heavy metals was observed by amendment of liquid manure, with exception of manganese in pot grown wheat and mercury in all plants.

Keywords: *analytical chemistry; environmental chemistry; arsenic; mercury;*

P-0582

PREPARATION AND CHARACTERIZATION OF MONOLITHIC STATIONARY PHASES FOR THE SEPARATION OF SMALL MOLECULES

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Monolithic stationary phases are composed of one piece of porous material which fills the whole space of capillary column. Organic polymer monoliths are prepared by radical polymerization inside the silica capillary. Polymerization mixture contains functional and crosslinking monomers, porogenic solvents and initiator of polymerization reaction. Optimization of the composition of the polymerization mixture allows easy control of separation and hydrodynamic properties such as porosity, efficiency and selectivity.

To increase efficiency of isocratic separation of low-molecular compounds the effect of applied crosslinking monomer in polymetacrylate monolithic columns was studied. Polymetacrylate monolithic columns containing lauryl metacrylate as functional monomer were prepared using crosslinking monomers with different lengths of methylene and oxyethylene chains between two metacrylate units. Generally used ethylene dimetacrylate crosslinker was replaced by tetramethylene, hexamethylene, dioxyethylene, trioxyethylene and tetraoxyethylene dimetacrylate. For example, substitution of ethylen dimetacrylate by tetraethylene dimethacrylate led to a significant increase in efficiency up to 71 000 plates/meter for benzene.

In order to increase the application range lauryl metacrylate was replaced by N, N-dimethyl-N-metacryloxyethyl-N-(3-sulfopropyl) ammonium betaine. Columns prepared with this functional monomer are suitable for application in hydrophilic interaction chromatography. Column prepared with zwitterionic functional monomer and dioxyethylene dimetacrylate as a crosslinking monomer provided efficiency of 69 000 plates/meter for thiourea and again confirmed the significant effect of chain length in crosslinking monomer to efficiency of monolithic capillary columns.

The optimized columns have been tested for reversed-phase and hydrophilic interaction separations of complex mixture of flavones and phenolic acids in one-dimensional and comprehensive two-dimensional liquid chromatography.

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Keywords: *liquid chromatography; polymers;*

P-0583

QUANTITATION OF SERTRALINE AND ITS METABOLITE BY HPLC IN PLASMA

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High rates of poor compliance and clinical heterogeneity of depression are main problems for the practical application of selective serotonin reuptake inhibitors (SSRIs). Main targets for the use of therapeutic drug monitoring (TDM) in depression pharmacotherapy are achievement of therapeutic ranges, confirmation of subtherapeutic concentrations in treatment non-responsive patients[1, 2]. Sertraline is a widely used antidepressant belonging to the SSRIs class.

The purpose of this study was to provide a fast and economic analytical method to determine sertraline (S) and its metabolite desmethylsertraline (DS) in plasma for the use of TDM applications.

Isolation of S and DS from plasma was carried out by solid phase extraction method with usage C-18 extraction cartridges (50 mg, 1 ml). These elutes were injected to Eclipse XDB-C18, 4.6 mm × 150 mm column. The column was eluted at 50 °C with a mobile phase of 45% acetonitrile and 55% NaH_2PO_4, pH 3,8 at a flow rate of 0.4 ml/min. Four different wave-length (200-205-210-215 nm) UV detection was applied.

The chromatogram of a drug-free sample showed stable base-line and only a few extraneous peaks, even at 200 nm. Calibration curves were linear in the range of 5-500 ng/ml for S and 10-750 for DS, all of them with coefficients of determination (r^2 values) ≥ 0.9500. High percent recovery values of S and DS were obtained. The optimal retention time for determining S and its metabolite DS in plasma were 8.5 min and 7.5 min, respectively. This method was successfully validated and applied to the determination of S and DS in plasma.

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P-0584

UTILIZATION OF CHIROPTICAL SPECTROSCOPY IN THE CLINICAL DIAGNOSIS OF ALZHEIMER'S DISEASE

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The number of people who have Alzheimer's disease is expected to grow as the population becomes older. Unfortunately, there is no reliable and non-invasive method for clinical diagnosis. As an improvement on molecular spectroscopy, we used chiroptical methods [ECD (electronic circular dichroism) and ROA (Raman Optical Activity)] to investigate the blood plasma[1] of healthy elderly controls and patients with Alzheimer's disease. The aim was to find specific spectral markers and develop a new method for early clinical diagnosis.

The ECD spectra were measured directly after thawing frozen samples and also after dilution them by a phosphate buffer in 0.01 mm quartz cuvette. Unfortunately, the blood plasma had a very strong fluorescence background in ROA; therefore, we tried to suppress it by the three different procedures: **i**) filtration by a 0.45 μm membrane filter, **ii**) addition of solid sodium iodide as a kinetic quencher, **iii**) sample blanching by a laser beam before the measurement. By using a combination of these procedures, fluorescence background was reduced ten times. Finally, the spectral baselines were improved by correction using of Fourier filtering.

Multidimensional statistical methods were used to evaluate the ECD and ROA spectra. After evaluation we got 4 groups of samples: healthy controls, mild dementia, moderate dementia and severe dementia.

Our preliminary results suggest that the human blood plasma can be successfully measured by both the ECD and ROA methods and these methods could be potentially useful for the clinical diagnosis of Alzheimer's disease.

Acknowledgement: *The work was supported by the Prague Operational Programme for Competitiveness (Grant No CZ.2.16/3.1.00/22197); the Ministry of Education, Youth, and Sports of the Czech Republic (Grant No MSM6046137307); the Czech Science Foundation (Grant No P208/11/0105); Specific University Research MSMT No 21/2012 - A1_FCHI_2012_003, A2_FCHI_2012_015.*

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Keywords: *Raman spectroscopy; Circular dichroism; Analytical Methods; Medicinal chemistry;*

P-0585

CHIROPTICAL SPECTROSCOPY OF HUMAN BLOOD PLASMA FOR POTENTIAL DIAGNOSIS OF COLON CANCER

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Colon cancer is after the breast cancer the most abundant cause of the cancer death in the world. The reason of high mortality is the fact that almost half of the colon cancers are detected at an advanced stage. Unfortunately, well-established clinical procedures as fecal occult blood test (FOBT) and the colon endoscopic examination have low reliability and sensitivity at an early-stage of the disease. Therefore, we used chiroptical methods – electronic circular dichroism (ECD) and Raman optical activity (ROA) – combined with Raman spectroscopy to investigate the human blood plasma[1] with the aim to find new specific spectral markers for minimally-invasive clinical diagnosis of the disease.

The ECD spectra of blood plasma samples from healthy controls and the colon cancer patients were measured after the dilution of plasma by a phosphate buffer (pH = 7.4). In the cases of ROA/Raman experiments, the undesirable fluorescence background of the plasma was suppressed by the combination of three different procedures: filtration by a 0.45 μm membrane filter, addition of solid sodium iodide as a kinetic quencher and sample blanching by a laser beam before the measurement.

The obtained spectra were evaluated by multidimensional statistical methods, which allowed distinguishing the blood samples of healthy controls and the colon cancer patients.

Acknowledgement: *The work was supported by the Prague Operational Programme for Competitiveness (Grant No CZ.2.16/3.1.00/22197); the Ministry of Health of the Czech Republic (Grant No NT13259); the Ministry of Education, Youth, and Sports of the Czech Republic (Grant No MSM6046137307); the Czech Science Foundation (Grant No P208/11/0105) and Specific University Research MSMT No 21/2012 - A1_FCHI_2012_003 and A2_FCHI_2012_015.*

References:

1. Michal Tatarkovic, Zdenek Fisar, Jiri Raboch, Roman Jirak and Vladimir Setnicka, *Chirality*, **2012**, in press

Keywords: *Analytical Methods; Cancer; Circular dichroism; Medicinal chemistry; Raman spectroscopy;*

P-0586

ESI-MS INVESTIGATION OF THE COMPLEXATION BEHAVIOR OF MACROCYCLIC THIACROWN ETHERS AND BIVALENT TRANSITION METALS

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Electrospray ionization mass spectrometry (ESI-MS) was used to study the complexation behaviour of three newly synthetized[1] thia-macrocycles with different 3d metal chlorides (i.e. $CuCl_2$, $CoCl_2$, $NiCl_2$, and $ZnCl_2$).

The study demonstrates that the thiacrown ethers preferentially bind traces of copper even in the excess of other metal ions. The binding process is accompanied by a reduction from Cu^{II} to Cu^{I} and the formation of $[(\text{thiacrown})Cu]^+$ species. By use of 18-crown-6 as a reference the absolute association constants are evaluated.

The reduction process was also studied with EPR spectroscopy. EPR data in solution show evidence for the ligand oxidation ($Cu^{II} + L \quad Cu^{I} + L^{+\bullet}$), moreover an interaction of the oxidized ligand with solvent molecules was observed.

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Keywords: *Copper; Electrospray ionization; Mass spectrometry; Macrocyclic ligands; Sulfur heterocycles;*

P-0587

DEVELOPMENT OF CARBONATE SENSOR BASED ON LN(III) COMPLEXES OF MACROCYCLIC LIGANDS

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The Ln(III) complexes of macrocyclic ligands (mostly DOTA derivatives) are often employed in medicinal chemistry as MRI agents (Gd) and luminescent probes (Eu, Tb, Yb, Nd in VIS/NIR range). DO2A (1,4,7,10-tetraazacyclododecane-1,7-diacetate) and DO3A (1,4,7,10-tetraazacyclododecane-1,4,7-triacetate) are hexa- and heptadentate macrocyclic ligands forming very stable complexes with lanthanide(III) ions where two and three, respectively, coordination sites are occupied by water molecules. These complexes form ternary species with small mono- and bidentate ligands (e.g. fluoride, acetate, phosphate, carbonate) and, therefore, these complexes are suggested as sensors for sensitive luminescence-based determination of above mentioned anions. In this contribution, the thermodynamics of association of $[Ln(H_2O)_2(DO3A)]/[Ln(H_2O)_3(DO2A)]$ (Ln = Eu, Tb) with chosen bidentate anionic ligands using luminescence spectroscopy was studied. The ternary [Ln(DO3A)(L)] and [Ln(DO2A)(L)] complexes (Ln = Eu, Tb, L = picolinate, isoquinoline-3-carboxylate) show improved photophysical properties due to the antenna effect of the these anions. High quenching effect of carbonate anion and, to a lesser extent also oxalate, enables construction of a linear calibration plot utilizing optimized experimental conditions for carbonate determination in solution. Both "on-off" sensors show a comparable sensitivity and the detection limit. The analysis of commercial samples of European mineral waters was carried out and confirmed no systematic error to the present analysis. The present analytical method is simple and rapid, and it is useful for sensitive determination of bicarbonate/carbonate concentration in water samples under aerobic conditions. Using organic ligands having similar spectral properties, this approach was modified and tested to get new "off-on" sensors operating in VIS region and the results will be presented.

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Keywords: *luminescent probe; anions; lanthanide complexes;*

P-0588

VOLTAMMETRIC DETERMINATION OF 5-NITROBENZIMIDAZOLE AT A BISMUTH FILM-MODIFIED GOLD ELECTRODE

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Bismuth film electrodes have become an attractive new subject of electroanalytical research as a potential replacement for mercury electrodes. In this work, the voltammetric behavior of the genotoxic compound 5-nitrobenzimidazole was investigated using direct current voltammetry (DCV) and differential pulse voltammetry (DPV) at a bismuth film-modified gold electrode (BiF-AuE). The bismuth film was deposited *ex situ* at a constant potential of –1.2 V (vs. Ag/AgCl (3 mol L^{-1}KCl)) for 300 s in a plating solution (1.0 g L^{-1} Bi(III) solution in 0.1 mol L^{-1} acetate buffer of pH 4.5) under stirring. The optimum conditions for the determination of 5-nitrobenzimidazole in the concentration range from 1 to 100 µmol L^{-1} were found in the medium of Britton–Robinson buffer of pH 9.0; the limits of quantification (L_Qs) were found to be 0.54 µmol L^{-1} (for DCV) and 2.0 µmol L^{-1} (for DPV). An attempt to increase the sensitivity using adsorptive stripping voltammetry at the BiF-AuE was not successful. The practical applicability of the newly developed methodology was verified for the direct determination of 5-nitrobenzimidazole in drinking and river water model samples, with L_Qs $\approx 10^{-6}$ mol L^{-1}.

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Keywords: *Analytical methods; Electrochemistry; Voltammetry; Bismuth; Thin films;*

P-0589

FULLY DELOCALIZED (ETHYNYL)(VINYL)PHENYLENE BRIDGED TRIRUTHENIUM COMPLEXES IN UP TO FIVE DIFFERENT OXIDATION STATES

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Within the field of organometallic mixed-valent chemistry, 1,4-diethynylphenylene has gained particular popularity as a bridging ligand because of the ready availability of the parent alkyne, its good ability to electronically couple the bridged sites and the stability it conveys to the oxidized forms. At the same time, the 1,4-diethynylphenylene ligand has turned out as an excellent example of Janus-headed behaviour with respect to Jorgensens original definition of a non-innocent ligand.[1]

Spectroscopic and cyclovoltammetric investigations on the triruthenium complex $[(dppe)_2Ru\{\text{-}C{=}C\text{-}1,4\text{-}C_6H_4\text{-}CH{=}CH\text{-}RuCl(CO)(P^iPr_3)_2\}_2]^{n+}$ suggest that this carbon-rich complex is an intriguing case of extended metal-organic p-systems exhibiting complete electron delocalization over three redox-active subunits in five well-separated redox states (n=0-4). The carbon rich ethynyl(vinyl)phenylene bridges are non-innocent redox-active ligands which actively participate in every redox process. Given the rather strong interest in understanding molecular wires[2], it seemed worthwhile to add gold-binding functional groups on the terminal moieties in order to gain valuable insight into the structure-property relationships of molecular wires with hole-conducting properties and low turn-on voltage.[3]

Herein we report the synthesis and our findings on the bis(ethynylvinyl)phenylene bridged trinuclear complexes*trans*-$[\{Ru(dppe)_2\}\{\text{-}C{=}C\text{-}1,4\text{-}C_6H_4\text{-}CH{=}CH\text{-}RuCl\ (CO)(P^iPr_3)_2\}_2]$, *trans* -$[\{Ru(dppe)_2\}\{\text{-}C{=}C\text{-}1,4\text{-}C_6H_2\text{-}2,5\text{-}(OMe)_2\text{-}CH{=}CH\text{-}RuCl(CO)\ (P^iPr_3)_2\}_2]$ and its corresponding derivative *trans*-$[\{Ru(dppe)_2\}\{\text{-}C{=}C\text{-}1,4\text{-}C_6H_4\text{-}CH{=}CH\text{-}Ru(\eta^2\text{-}O_2CC_6H_4SAc)(CO)(P^iPr_3)_2\}_2]$ with respect to charge and spin delocalization. The terminal 4-mercaptobenzoate ligands of *trans*-$[\{Ru(dppe)_2\}\{\text{-}C{=}C\text{-}1,4\text{-}C_6H_4\text{-}CH{=}CH\text{-}Ru(\eta^2\text{-}O_2CC_6H_4SAc)(CO)(P^iPr_3)_2\}_2]$ bind to gold electrodes and should allow for measuring molecular conductivities.

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Keywords: *cyclovoltammetry; spectroelectrochemistry; molecular wires; organometallic mixed-valent chemistry; Ruthenium;*

P-0590

SILICON DETERMINATION IN NICKEL SUPERALLOYS BY ICP-AES METHOD

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Silicon is impurity in heat-resistant Ni alloys such as Inconel and determinate in ranges from 0,001 to 0,2 % wt, whereas at Si content from 0,5 to 2 % wt silicon reduce erosion. In nickel brazing (Solbraz, Nicrobraz, Colmonoy) silicon exclude erosion of brazed alloy at Si content more than 5 % wt.

This work deals with of method of sample preparation and test method of Si analysis from 0,001 to 10 % wt in Ni alloy by using ICP-AES method.

It's known Si with HF forms volatile compound SiF_4; under the influence of HF Si is washed away from glass spray system of spectrometer; Si is adsorbed on plastic spray system of spectrometer; in mixture of HCl and HNO3 silicon precipitate into silica sol $(H_2SiO_3)_n$. Therefore two ways of a sample preparation and determination of silicon were offered.

The first way consists in alloy dissolution in the minimum quantity of chlorazotic acid diluted with water in ratio 1:10. The second way consists in alloy dissolution in the minimum quantity of a mixture of H_2O, HCl, HNO_3, HF (in ratio 10:3:1:1). Alloy samples are dissolved by using microwave digestion system MARS5. Measurements of Si content carried out on ICP-AES spectrometer VARIAN 730 ES in reference materials. At first way quartz spray system was used, at second - fluoroplastic spray system, a plastic spray.

It's shown that this way allows to determinate silicon in a range from 0,001 to 3 % wt with error no more than 3 % relative by using first way and in a range from 0,1 to 10 % wt with an error of no more than 5 % relative by second one.

The proposed ways of Si analysis can be successfully applied in the silicon determination in alloys based on iron, cobalt, titanium, copper, etc.

Keywords: *silicon analysis; ICP-AES; test method; Ni alloys;*

P-0591

SELECTIVE DETECTION OF PROTEINS IN SDS-PAGE ANALYSIS

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SDS-PAGE is a widely used technique when dealing with biomacromolecules. The most used proteins detection techniques nowadays in SDS PAGE analysis are Coomassie brilliant blue stain and silver stain; both techniques allow to detect proteins in gels with good sensitivity and reasonable time consumption. When analysing complex mixture of proteins selectivity is often desired. Even if well-established techniques are available for this purpose (such as western blotting and post-translational modifications selective probes), the development of new, cheaper and faster methods to selectively detect proteins is of great interest.

Several compounds showing affinity towards different kind of functional groups which are present in amino-acids side chains (e.g. phosphorylated sites[1], imidazole ring[2], carboxylates[3]) have been reported in literature.The structure of such compounds consists of Zn(II) or Cu(II) coordination complexes as recognition moiety combined with a reporting fluorophore. Binding activity leads to changes in fluorescence, such as variation of intensity or emission wavelength shift, allowing detection.

By mean of the same strategy, we designed different potential probes consisting of Zn(II) – cyclen complex covalently linked to fluorescent dyes such as nile blue, hodamine B and eosin Y. We are currently synthesizing such compounds, which will be tested as probes for selective recognition of consecutive negatively charged aminoacids sequences (e.g EE, DD, EED etc.) in model proteins.

As different approach, we are going to use known specific interactions between metal cations and given amino acid sequences, followed by detection of bound cations (e.g by colorimetric indicators). The detection of polihistidine-tagged proteins by using the interaction with copper(II) cations is currently under investigation.

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Keywords: *molecular recognition; electrophoresis; fluorescent probes;*

P-0592

ELECTROOXIDATION OF NA+/K+-ATPASE AFTER SOLUBILIZATION BY OCTAETHYLENE GLYCOL MONODODECYL ETHER

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The present study is focused on oxidation and adsorption behaviour of full-length transmembrane protein Na+/K+-ATPase (NK) and its water-soluble isolated cytoplasmic loop connecting transmembrane helices 4 and 5 (C45) using voltammetric methods. Membrane proteins are substances that are poorly soluble or insoluble in aqueous solution. The C45 is soluble in water, the nonionic surfactant octaethylene glycol monododecyl ether was used for NK solubilization[1]. Both proteins, NK and C45, were studied using adsorptive transfer cyclic voltammetry and square-wave voltammetry on basal-plane pyrolytic graphite electrode. While NK gives two oxidation peaks (peak Y: +0.55 V and peak W: +0.7 V) related to tyrosine (Y) and tryptophan (W) oxidation, C45 is characterized by substantially lower anodic responses (peak Y&W: +0.65 V). High anodic currents of Y and W of NK are related to its transmembrane part, which are very rich in Y and W residues. These experimental procedures allow studying oxidation of NK and C45 at femtomole level without the necessity to use derivatization, labeling by electroactive markers or techniques based on protein immobilization within lipid bilayer attached to the electrode surface.

Acknowledgments: *The research was support by the internal grant LF UP (LF_2012_010), MZ CR (NT11071) and GA CR (303/09/H048).*

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P-0593

THE APPLICATION OF HPLC WITH ELECTROCHEMICAL DETECTION FOR THE DETERMINATION OF PESTICIDE CHLOROTOLURON

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Many herbicides are used in agriculture all over the world. Despite their benefits in increasing agricultural production, herbicides can have a negative impact on the environment and can pose a risk to animals and humans. For these reasons, there is a growing demand for fast and reliable pesticide monitoring in agriculture.

A method for the determination of phenylurea herbicide chlorotoluron was developed using reversed-phase HPLC with amperometric detection on carbon paste electrode in wall-jet arrangement. Separation and detection conditions for the determination were optimized, namely pH of mobile phase and detection potential. The optimum conditions for the determination are: LiChroCART® 125-4 Purospher® RP-18 (5 μm) column, mobile phase consisting of methanol and ten times diluted Britton-Robinson buffer pH 4.0 (60:40, v/v), and detection potential +1.3 V. Concentration dependences are linear in the range from $1.0 \cdot 10^{-7}$ mol L^{-1} to $1.0 \cdot 10^{-4}$ mol L^{-1} and the limit of determination reaches value of $1.1 \cdot 10^{-7}$ mol L^{-1}. The method was applied on model samples of river water, with the limit of determination for amperometric detection $1.9 \cdot 10^{-7}$ mol L^{-1}.

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Keywords: *Electrochemistry; Environmental chemistry; Liquid chromatography;*

P-0594

GOLD AND SILVER NANOPARTICLES MODIFIED BY RECEPTORS FOR ANIONS RECOGNITION

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Development of receptors which are designed foranoint recognition is an important branch of chemistry. The design of syntheticreceptors for selective sulfate over phosphate recognition in aqueous media hasbeen a significant challenge. Many of these compounds are not soluble in water.This problem can be solved by immobilization on the nanoparticles surface.

Nanoparticles were prepared by methodbased on the reduction of noble metals salts by reduction agents. The immobilizationsof polymethinium salt and two porphyrin-brucine derivatives were carried outby two different ways of ionic interaction. First, direct immobilization of selectormolecules on nanoparticles, second, immobilization of selector molecules on 3-mercaptopropionicacid premodified nanoparticles. Such prepared nanoparticles were characterizedby UV-Vis spectroscopy. This method was used for study of interactions of anionswith the modified nanoparticles in water.

Immobilization on nanoparticles, insome cases, prevents the selector molecules from aggregation in water. Variousspectral changes were observed in experiments with free versus immobilizedselectors in water depending on a type of used system and selected anions. The resultsshowed that type of used nanoparticles have positive or negative affected to stabilityof these systems in water and have a strong influence on their interactions.

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Keywords: *Anions; Nanoparticles; UV/Vis spectroscopy;*

P-0595

CHEMICAL COMPOSITION OF DIFFERENT OREGANO (ORIGANUM VULGARE L.) ESSENTIAL OILS: RELEVANCE FOR THE ACTIVITY AGAINST FOODBORNE AND SPOILAGE BACTERIA

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Herbs and spices have been used for centuries in culinary for seasoning and flavouring purposes. More recently, there has been a growing interest regarding the use of some plants and its essential oils (EO) for their activity against foodborne pathogens and foodspoilage bacteria. Due to its potential in extending the self-life of foods and its better acceptability by consumers who demand more “natural” foods, the use of EO can be an interesting alternative to substitute, at least partially, synthetic preservatives.

Oregano EO has been reported to possess a broad antimicrobial activity spectrum. Nevertheless, its activity is strongly dependent on the chemical composition which is known to differ with plant genotype, geographical origin and environmental conditions. Considering that most works focus on wild oregano but nowadays most is cultivated and sold in supermarkets, in this study we evaluated the chemical composition and antibacterial activity of commercially available oregano EO (EO1) and the EO extracted by hydrodistillation from oregano purchased from an aromatic plants supplier (EO2). The chemical profile of the essential oils, determined by gas chromatography-mass spectrometry (GC-MS), was very different with EO1 presenting carvacrol (68.3%), *p*-cymene (4.2%), thymol (3.8%) and gamma-terpinene (3.7%) as main compounds, while terpinen-4-ol (24.8%), *p*-menth-2-en-1-ol (13.9%), *p*-cymene (8.8%) and gamma-terpinene (7.4%) were the major ones in EO2. The antibacterial activity was determined against 7 Gram-positive and 3 Gram-negative bacterial strains by agar-diffusion method. Both oils inhibited all tested strains but the antibacterial activity was stronger for commercial EO with some strains presenting inhibition halos two times higher. This can be mainly ascribed to the higher content of phenolic derivatives, such as carvacrol and thymol, in EO1. These results demonstrate that oregano EO can be used for its antimicrobial effect against foodborne pathogens. Nevertheless, for this purpose it should be carefully chosen regarding its chemical composition.

Keywords: *Gas chromatography; Biological activity; Mass spectrometry; Natural products;*

P-0596

STUDY OF HEAVY METAL AND ESSENTIAL OIL CONTENT IN VARIOUS SPICES

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A spice is a dried seed, fruit, root, bark, or vegetative substance primarily used for flavoring, coloring or preserving food. Sometimes a spice is used to hide other flavors.A spice may be available in several forms: fresh, whole dried, or pre-ground dried. Generally, spices are dried. A whole dried spice has the longest shelf life and small seeds, such as fennel and mustard seeds, are used both whole and in powder form.

The flavor of a spice is derived in part from compounds that oxidize or evaporate when exposed to air. Grinding a spice greatly increases its surface area and so increases the rates of oxidation and evaporation. Thus, flavor is maximized by storing a spice whole and grinding when needed. The shelf life of a whole spice is roughly two years; of a ground spice roughly six months. The "flavor life" of a ground spice can be much shorter. Ground spices are better stored away from light.

In this study we analyse concentration of As, Hg, Pb and Cd and oil content in five spieces (origano, red and black pepper, coriander and anis) from three producer from serbian market. Analysis of hazardous metals were done by grafite furance AAS technique for Pb and Cd and by hydride techique for As and cold vapor for Hg, and essential oil content was determined by ethanole extraction. Amount of hazardous metals was bellow concentration estimated by serbian regulation.

Keywords: *Analytical Methods;*

P-0597

AUTHENTICATION OF ROMANIAN RIPENED BRINE CHEESE AND YELLOW CHEESE USING 1H-NMR SPECTROSCOPY AND GC-MS TECHNIQUE

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Romanian ripened brine cheese, traditionally called "Teleme" cheese, represents 60% of all kinds of cheese produced in Romania[1]. Teleme cheese is a soft white-brined cheese with many similarities with Feta cheese.[2]

The aim of this work was to establish whether fatty acids composition data obtained by ^{1}H-NMR and GC-MS can be used in the discrimination of traditionally Romanian ripened brine cheese as well as yellow cheese according to variety (goat, sheep and cow).[3, 4]

Characterizations of the lipid fraction of Romanian varieties of cheese samples were performed by ^{1}H-NMR spectroscopy and GC-MS methods. Based on the integral values of the signals from the ^{1}H-NMR, the fatty acid composition of traditionally romanian cheese samples was calculated[5]. Statistical analyses of the spectral data by mean of *Principal Component Analysis* (PCA) allowed that varieties of cheese to be discriminated.

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Keywords: *white-brined cheese; Teleme; Principal Component Analysis; 1H-RMN; GC-MS;*

P-0598

PH EFFECTS ON THE PHYTOCHEMICAL COMPOSITION AND ANTIOXIDANT ACTIVITY OF PROCESSED PEACH

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Adjustment of pH is often made in processed fruit products to assure food safety or the stability or functionality of ingredients or additives (e.g. pectins or sorbate). The objective of the work was to assess the effect of pH on relevant markers of functional and nutritional properties (antioxidant activity, phenolics and carotenoids) of processed peach puree. Clingstone peach [*Prunus persica* (L.) Batsch 'Catherine'] fruits were reduced to puree and the pH adjusted to 2.5; 3.0; 3.5; 4.0 and 4.5 with citric acid and sodium phosphate. Purees were then heated in water-bath at 90 ºC for 10 minutes and subsequently stored during 90 days at 4.5 ºC and at 23 ºC. Hydrophilic extracts were obtained with 80% methanol and carotenoids were extracted as described by Lavelli *et al.* (2009). Total antioxidant activity was assessed by the ABTS method, total phenolics by Folin Ciocalteu's method, and total carotenoids by spectrophotometery. Individual phenolics and carotenoids were separated and indentified by HPLC-DAD. After 90 days storage the total antioxidant activity, total phenolics and total carotenoids decreased, by 45%, 30%, and 47%, respectively (average of both temperatures). The decline was faster at 23 ºC than at 4.5 ºC, but the rate was not affected by pH. Levels of neochlorogenic and chlorogenic acid (7 and 11 µg/ g fw respectively) were lower at pH 4.0 or 4.5 than at lower pH values. Zeaxanthin, β-cryptoxanthin and β-carotene levels decreased more during storage at pH 2.5 and 4.5 (70%, 47%, and 45%, respectively), than at the intermediate pH values. In conclusion, puree pH, in the range 2.5 to 4.5 does not affect the overall antioxidant activity, but the kinetics of changes in the extractability of chlorogenic and neochlorogenic acids and zeaxanthin

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Keywords: *Antioxidant activity; Carotenoids; Peach processing; Phenolics;*

P-0599

ENCAPSULATION OF QUERCETIN WITH PROTEIN AND PROTEIN-STEARIC ACID MIXTURE COATING MATERIALS AND DETERMINATION OF TOTAL ANTIOXIDANT CAPACITY USING CUPRAC METHOD

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Microencapsulation method has been widely used in food industry in recent years. Retarding degradation of food additives, it causes expanded shelf life and controlled releasing of core materials through gastrointestinal system. Coating of surface takes place via secondary interaction between internal and external phase. Frequently encountered coating materials are cellulose derivatives, starch derivatives, and algynates etc. Coating antioxidant core with protein causes enhancing antioxidant efficient. Proteins have two important roles: They reduce surface tension at interface during emulsification and form macromolecular layer. Gelatin is a protein used widely in encapsulation process because of its excellent film-forming properties.

At the first step in this study, quercetin was used as internal phase and gelatin was used as external phase. After wall and core material was reacted each other at fixed wall/core ratio, formed microcapsules were powdered using freeze dryer. The minimum mixing time and optimal wall/core ratio was found as 4 h and 1:1 respectively. At the second step, gelatin and stearic acid mixture will be used as external phase.

After DSC analysis and cold-stage microscopy determination and particle size measurement, surface characterization of microcapsules will be achieved. And also, encapsulation efficient and shelf life analyses and invitro digestion experiments in synthetic saliva, stomach, and intestine liquids will be performed. Antioxidant capacity will be quantitatively determined using CUPRAC method in all experiments. In this way, optimal wall matrix, wall/core phase ratio and shelf life will be designated for microcapsules which core retention is accomplished without reducing in their total antioxidant capacity.

Keywords: *antioxidants; polymers; UV/Vis spectroscopy; Analytical methods;*

P-0600

MONITORING OF FUNGICIDES EFFECT ON THE PRODUCTION OF T-2 TOXIN

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The aim of the work was monitoring of fungicides effect on the production of T-2 toxin. Detection of toxigenic fungi was performed in malt houses and on barley seeds. *Fusarium* fungi are producers of a wide range of mycotoxins e. g. T-2 toxin, deoxynivalenol and zearalenone. T-2 toxin is trichothecene mycotoxin. The intoxication are especially in people with lowered immune system or weakened animals after ingestion of contaminated cereals. For this reason, set the limits that determined the maximum level of mycotoxins in cereals. The PCR method for confirmation of *Tri5* gene which encodes the production of trichothecene mycotoxins were performed for all tested strains of *Fusarium*. PCR were performed for 172 strains of *Fusarium* isolated from real samples. The gene was proved for 44 strains of *Fusarium*. Nutritive media were preparate with different concentration of tested fungicides (Polyversum, Horizon 250 EW, Falcon 460 EC and Bioan) and inoculated with *Fusarium* fungi, then incubated under various conditions. The content of T-2 toxin was determined by Agra Quant® T-2 toxin Test kit and HPLC. Our experiment showed that low concentration of fungicedes resulted in the increased production of T-2 toxin.

Acknowledgements: *This work was supported by MSM 0021627502 and project of University of Pardubice No. SGFChT07/2012.*

Keywords: *Fusarium; T2 toxin; ELISA method; fungicide;*

P-0601

ANALYSIS OF MUSHROOM TOXINS BY LIQUID CHROMATOGRAPHY – MASS SPECTROMETRY (LC-MS/MS)

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Background: Mushroom poisoning usually results from the consumption of wild poisonous species, which were misidentified and consumed because of their resemblance in colour and general morphology with edible mushrooms. Some common symptoms of mushroom poisoning include gastrointestinal upset such as vomiting and diarrhea. However, there are a number of known mushroom toxins which may cause death to victims if no proper or delay in treatment is given. For example, consumption of a single piece of mushroom containing high level of amanitins toxins may cause death of an adult [1, 2]. Poisonous mushrooms accidentally leaked into the food markets may induce multiple outbreaks of food poisoning cases. With early identification of the toxins presented in the questioned food items could not only be useful for stopping the spreading of further cases, but also help physicians in finding suitable treatment for the victims.

Method of Analysis: In this work, a quick and reliable analytical method for analyzing 5 mushroom toxins including the α, β, γ-amanitin, phallacidin and phalloidin using Liquid Chromatography – Mass Spectrometry (LC-MS/MS) is developed. A simple extraction and clean-up procedure is employed. The extract can be analyzed directly by LC-MS/MS in the Multiple Reaction Monitoring (MRM) mode. The method is capable of measuring mushroom toxins in food remnants down to 250µg/kg. Quantification and confirmation criteria are based on EC Directive 2002/657/EC. The mean spike recoveries of the 5 toxins fall within 88 to 109% with RSD ranging from 2.6 to 13%. The method is validated using a genuine dried specimen of *Amanite exitialis*, which is also known as the Guangzhou Destroying Angel. The cap and stipe of the specimen are found to contain high levels of α, β-amanitin and phallacidin.

Application to Practice: The method has been used to assist the World Health Organization (WHO) in the investigation of a fatal mushroom poisoning case occurred in Laos in May 2011. The results revealed that one of the samples contained lethal levels of α, β, γ-Amanitin and Phallacidin, indicating that the item was not suitable for human consumption.

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Keywords: *Liquid chromatography; Mass spectrometry;*

P-0602

SIMULTANEOUS SCREENING AND DETERMINATION OF PHTHALATES, SUCH AS DI (2-ETHYLHEXYL) PHTHALATE (DEHP), DIBUTYL PHTHALATE (DBP), BUTYL BENZYL PHTHALATE (BBP) IN FOOD CIRCULATED AT KOREAN MARKET USE BY GC/MS

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Known as environmental contaminants phthalates have been detected in various types of retail foods. Consumer's exposure to phthalates is common so that are concerned about chemicals in food. This study has been conducted to determine 3 kinds of phthalates, such as di (2-ethylhexyl) phthalate (DEHP), dibutyl phthalate (DBP), butyl benzyl phthalate (BBP) which are extracted from processed food groups(sugar, soybean oil, red pepper paste etc). We first established validated methods. Standard phthalates were analyzed with hexane or acetonitrile and quantification was carried out using Gas-Chromatography in combination with Mass spectrometry detector(GC/MS) in electronic ionisation mode(EI) with selected ion monitoring(SIM). The base peak of all three phthalates was identified as $m/z = 149$ while characteristic ions, 223, 205 for DBP; 206, 91 for BBP; 167, 279 for DEHP were identified. Base peak will be used for screening and specific ions for quantitative studies. Limits of detection range for DEHP, DBP, and BBP was 2 ~ 10 ng/mL, repectively. The calibration curves for 3 phthalates showed linearity in the range 0.990 ~ 0.999. Currently, we are applying this method to the processed foods for monitoring project. The results should provide useful information to guarantee food safety.

Keywords: *Phthalates; monitoring; DBP; BBP; DEHP; GC-MS(EI-SIM);*

P-0603

TIN AND ALUMINIUM LEVELS IN INFANT FORMULAS

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Infant formula serve as substitutes for human milk and play a particular role in diets. Unlikely breast milk, artificial formula can contain several contaminants with toxic heavy metals and pesticides that carry potential health problems to infants. Infants are particularly sensitive to the effects of ingested toxicants as food consumption is greater on a body-weight basis.

At the present, the Korean standards of tin and aluminium in infant formula are not established.

This research was carried out to monitor the levels of tin and aluminium in infant formula distributed in Korean markets. The infant foumulas were analysed by ICP-MS after microwave-assisted digestion. The performance characteristics of ICP-MS were determined in terms of linearity, precision, recovery, limit of detection(LOD) and limit of quatification(LOQ). As a result, LOD and LOQ of powdered infant formula were 0.2ppb, 0.6ppb for tin and 2.8ppb, 9.2ppb for aluminium. The recoveries by standard addition were 88.4~110.0% for tin and 93.1~112.7% for aluminium. These results will be used as a fundamental database to set up the Korean standards of tin and aluminium in infant formula.

Keywords: *Tin; Aluminium; Infant formula;*

P-0604

PREPARATION OF SOY SAUCE LOW IN SODIUM CHLORIDE

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These days, people’s interest forcuses on health, and particularly the exsessive intake of table salt has received tremendous attention resulting in an increased demand for low NaCl-containing foods. Soy sauce, which is the Japanese representative seasoning, has a large amount of NaCl. In this study I attempted to decrease the NaCl content of the soy sauce whithout spoiling the flavor. Soy sauce contains 15-18% NaCl and 1-2% monosodium glutamate and is a traditional seasoning with salty and umami tastes as the core of the tasting characteristics. The low NaCl-containg soy sauce used in this study was prepareed by using a pre-soy sauce with an NaCl content 0.5 time the NaCl content of conventional soy sauce obtained by the short term fermentation method developed by Muramatsu et al. as the base material, and by adding a variety of amino acids and peptidic saltiness-enhancing substances such as Lys/HCl, Gly-OEt/HCl, and Orn-Tau/HCl which were developed by our laboratory. Based on the respective threshold values, intensities of salty and umami tastes were represented quantitatively in scores for sensory analysis. By using the scores the tasting characteristics of low NaCl-containing soy sauces to which were added various saltiness-enhancing substances were compared. The results revealed that commercial soy sauce was an ideal food in that it possessed well balanced intensities of salty and umami tastes. The balance of salty and umami tastes in the Orn-Tau/HCl added low NaCl-containing soy sauce was close to that of the commercial soy sauce. The low NaCl-containing soy sauce to which KCl, a long used substitute of NaCl, was added showed too strong of a umami taste that killed the effect of salty taste.

Keywords: *bioorganic chemistry; material science; peptides; salt effect; sodium;*

P-0605

MONITORING ANTI-IMPOTENCE DRUGS AND ITS ANALOGUES IN FOODS

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Illegal compounds such as drugs and its synthetic analogues have been detected in foods until a recent date in Korea. Especially, unknown compounds that have the modified chemical structure of anti-impotence drugs such as sildenafil, tadalafil and vardenafil were frequently detected in various foodstuffs. Illegal compounds(benzylsildenafil, aminotadalafil, hydroxyvardenafil etc) that have modified chemical structure of the drugs have been used to avoid the government inspection. The adulteration of foods with drug analogues is potentially dangerous for human health because it is not proved their safety at all. In order to ensure food safety, we investigated the actual condition of the suspected samples and monitored about 40 retail foods. Three simultaneous analytical methods were established using LC/PDA and confirmed with LC/MS for 35 analogues and 5 anti-impotence drugs. Anti-impotence drugs and its analogues were detected in 5 samples. Tadalafil was detected in an sample. Icariin was detected in 3 samples. Yohimbine was detected in 3 samples.

Keywords: *Illegal compounds; Anti-impotence drugs; monitoring; LC/MS; LC/PDA;*

P-0606

DETERMINING 4-METHYLIMIDAZOLE IN CARAMEL COLOR BY CAPILLARY GAS CHROMATOGRAPHY

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As a color additive, Caramel color is the world's most widely consumed food coloring ingredient. Caramel color contains 2-methylimidazole and 4-methylimidazole, both of which may cause cancer in laboratory animals. For such reason, the 4-methylimidazole content of caramel color, a food additive, is controlled in the EU, US(FCC), Japan, and Korea.

The quantitative analysis of the 4-methylimidazole used in Korea's Food Additive Code and US's FCC (Food Chemical Codex) is a somewhat old-fashioned gas chromatography using column packing of 7.5% Carbowax 20M +2% KOH.

For the aforesaid reason, a method of determining 4-methylimidazole in caramel color via capillary gas chromatography was studied. The method consisted of methylene chloride extraction of the sample followed by concentration and GC analysis.

GC analysis was performed using HP-20M, Carbox 20M, HP-5 capillary column (0.32?, ID?25M), and hydrogen flame-ionization detector. As internal standard material, 2-methylimidazole was used.

The linear range was 0.08~1.6?/L, and the limit of detection was 0.04 ?/L. The average recoveries were 90.4~98.0%, and the relative standard deviations were 0.8 ~2.5%. Consequently, 4-methylimidazole contained in caramel color was analyzed using the capillary column, which is currently used widely.

Keywords: *4-methylimidazole; Caramel; Gas Chromatography; Capillary;*

P-0607

DIRECT MONITORING OF MYOGLOBIN-CATALYZED LINOLEATE PEROXIDATION BY FOURIER TRANSFORM INFRARED SPECTROSCOPY

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Lipid peroxidation reactions are a major concern in Food Science. These reactions represent a main part of the degrading processes taking place in food products resulting in changes in flavor, color, texture and producing cytotoxic and genotoxic compounds. Myoglobin has been demonstrated to catalyze lipid peroxidation in biological tissues and muscle-based foods. In this work we have employed UV/Vis and Fourier transform infrared spectroscopies to study the mechanism of myoglobin-catalyzed linoleate per oxidation. The UV/Vis spectra of the reaction of linoleate with met-myoglobin and with ferry-myoglobin show characteristic transitions at 235 nm and 285 nm indicating the formation of primary and secondary oxidation products. Ferryl-myoglobin is potent in inducing linoleate peroxidation independent of the linoleate/Mb ratio, while met-myoglobin has been found to be an effective catalyst only in high ratios (1:300). We have also monitored the reactions using Fourier Transform Infrared spectroscopy. During the reactions the decreasing intensity of marker linoleate vibrations and appearance of new vibrations in the 1700–1600 cm^{-1} and 1500–900 cm^{-1} regions that can be attributed to linoleate primary and secondary oxidation products have allowed us to directly monitor the process of linoleate peroxidation. Concurrent changes in the secondary structure of myoglobin are observed through amide I and amide II modes. The antioxidant activity of vitamin C has been investigated and will be discussed.

Keywords: *Oxidation; Proteins; Lipids; IR spectroscopy; UV/Vis spectroscopy;*

P-0608

METABONOMICS OF TABLE GRAPES: FROM METABOLIC PROFILES MONITORING TO CLASSIFICATION OF GRAPES BY EXPERT INFORMATIC SYSTEMS

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Table grapes are food products of considerable commercial value for several countries (USA, Brazil, Italy, South Africa, China, Chile, India and Australia are the most important producers). In Europe, Italy ranks first place for table grape production with more than eight million tons per year (ISTAT, 2011).

Recently, we developed an innovative analytical method for the characterization of various table grape cultivars. In our study, multivariate statistical analysis applied to ^{1}H NMR data of table grapes, revealed that the inter-vineyard variability of the metabolic profile has a greater discriminating effect over the intra-vineyard one.[1]

This presentation deals with the effects of several agronomical practices on the metabolic profile of the table grapes during different production stages. The variation of the metabolic features of the grapes was followed by ^{1}H NMR spectroscopy. Moreover, ^{1}H NMR spectra of ripe table grapes were processed to be used as input for expert classification systems based on three different algorithms: J48, Random Forest and an Artificial Neural Network performed with the Error Back Propagation procedure. The performances of the three algorithms in the discrimination of grapes on the bases of some common features (variety, vintage, use of plant growth regulators, trunk girdling, vineyard location) will be shown.

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Keywords: *NMR spectroscopy; metabolism;*

P-0609

AUTHENTICATION OF FOURTEEN ROMANIAN GRAPE SEED OIL VARIETIES USING SPECTROSCOPIC METHODS

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Grape seed oil proved to be a much appreciated ingredient in food as well as in cosmetics[1]. Its specific composition in polyunsaturated fatty acids and the content of tochopherols and polyphenols makes the grape seed oil a nutraceutical product[2].

In this study ^{1}H-NMR spectroscopy and systems of chemometrical equations were used to determine the composition of grape seed oils on four classes of fatty acids[3]. Using Principal Component Analysis (PCA) applied to the spectral information, grape seed oils were discriminated based on their variety and harvest time.

^{1}H-NMR spectral information was used to determine the composition of grape seed oils obtained from 14th different varieties of Romanian grapes (Burgundy, Cabernet Sauvignon, Muscat Ottonel, Feteasca Neagra, Feteasca Regala, Pinot Noir, Pinot Gris, Columna, Cristina, Chardonnay, Mamaia, Merlot, Riesling Italian collected from Murfatlar vineyard). Several compositional differences have been noticed. The compositional differences among the grape seed oils varieties becomes important when decision about the field of application is made.

PCA statistical processing of the data obtained by NMR and IR spectroscopy applied directly on the triglycerides, allowed a better discrimination of grape seed oils on the bases of variety[4].

All triglycerides from the grape seed oil samples were subjected to esterification reaction and the resulted FAME were analysed by means of GC-MS standard method.

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Keywords: *Grape seed oil; Principal Component Analysis; 1H-NMR; GC-MS; Composition;*

P-0610

POST COLUMN DERIVATIZATION METHODS FOR THE DETERMINATION OF MYCOTOXINS IN FOOD PRODUCTS AND FEED MATERIALS BY LIQUID CHROMATOGRAPHY WITH FLUORESCENCE DETECTION

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Mycotoxins are a group of toxic compounds, produced as secondary metabolites by organisms of the *fungus* kingdom. Some of the health effects found in animals and humans include mutagenic, carcinogenic and teratogenic effects, kidney and liver damage, neurotoxicity, gastrointestinal hemorrhage, immuno suppression and even death. In Europe maximum residue limits of the most toxic mycotoxins have been set, based on their toxicity and on the frequency of potentially contaminated foodstuffs. In the last decade liquid chromatography coupled with tandem mass spectrometric detection has gained more importance for multi-analyte mycotoxin determination, assuring accurate and sensitive determinations. Anyway, as underlined in European Decision 2002/657, chromatographic methods based on fluorescence detection represent a valid alternative as confirmatory methods in official control analyses, providing good results in terms of selectivity, sensitivity, instrumental costs and simplicity.

Only a limited number of mycotoxins have natural fluorescence on their own; however most of mycotoxins lack of any significant chromophores, hence for a sensitive detection a derivatization step is required to convert them into fluorescent derivatives. Thus, liquid chromatography methods for the determination of mycotoxins are based on reverse-phase separations and fluorescence detection, coupled with pre- or post-column derivatization.

The chemical post-column derivatization allows to overcome drawbacks and disadvantages due to pre-column techniques, such as low sensitivity, matrix-related limitations, use of toxic reagents, instability of fluorescent derivatives and slow reaction kinetics.

In this study analytical methods based on post-column derivatization for the determination of aflatoxins (B_1, B_2, G_1 and G_2), fumonisins (B_1 and B_2) and trichotecenes deoxynivalenol (DON) and nivalenol (NIV) in foods and feed materials are presented. Separation experimental conditions, the sample extraction and clean-up and validation performances were carefully evaluated, shooting for developing fast and selective methods for high throughput applications in risk-assessment studies and control analyses.

Keywords: *liquid chromatography;*

P-0611

THE APPLICATION OF DIFFERENT DETECTION METHODS FOR IRRADIATED FOODS BY TL, PSL, ESR AND GC/MS

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Food irradiation, treatment of foods with ionizing radiations such as gamma rays, X rays and electron beams, is technique that do not modify nutritional properties of irradiated food, do not produce toxical effects and do not induce radioactivity in food itself. It can be used to prevent food contamination and to extend its shelf life.

To set up applicability for foods which are not allowed to be irradiated in Korea, we have investigated 6 food groups including dried fruits and seeds. Samples were analysed by thermoluminescence(TL), photostimulated luminescence(PSL), electron spin resonance(ESR) method before and after gamma irradiation. And in case of seeds were applied by gas chromatography/mass spectrometry(GC/MS) method.

The present work showed that TL method was a sensitive to identify irradiated foods and PSL was a suitable method for screening of irradiated foods. ESR was a very useful qualitative method, because of small sample size and no solvent consumption. Detection of hydrocarbons by GC/MS was applicable for identifying post-irradiation of samples. As a result, this study may help that consumers is able to make their own choices between irradiated and non-irradiated foods.

Keywords: *Irradiated foods; Thermoluminescence; Photostimulated luminescence; Electron spin resonance; Gas chromatography/Mass spectrometry;*

P-0612

STUDY ON ANALYTICAL METHOD OF LIQUID PARAFFIN IN FOODS

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Liquid paraffin is a mixture of heavier alkanes derived from petroleum. Liquid paraffin can be used as a lubricant in processing machinery, a coating agent for fruits and a releasing agent. There is a growing interest in food contaminated with liquid paraffin. The purpose of this study is to develop the analytical method of liquid paraffin in foods. To develop the time and cost effective method, gravimetric analysis and gas chromatography-flame ionized detector(GC-FID) were compared. Recovery tests were performed in cakes, capsules and dried fruits. Liquid paraffin was extracted by hexane and purified by alkaline permanganate oxidation and passing through a silica cartridge. GC-FID method was validated for liquid paraffin by measuring the limit of detection(LOD), the limit of quantification(LOQ) and the linearity of calibration curve. The amount of liquid paraffin in foods was determined by using the optimized analytical method.

Keywords: *Food additive; Liquid paraffin; Anayltical method;*

P-0613

NON PROTEOLYTIC AMINOACYL DERIVATIVES IN CHEESES

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Cheeses are complex mixtures of amino acids, peptides and proteins, mostly derived from the proteolysis of the caseinic fraction precipitated in the curd during cheese production. In the last years several studies have demostrated that small aminoacyl dipeptide-like derivatives of non proteolytic origins are present in not negligible amount in several cheeses, like Parmigiano-Reggiano, Grana Padano and Asiago[1, 2]. These compounds were identified as gamma-glutamyl-amino acids, lactoyl-lamino acids and pyroglutamyl-amino acids, and collectively named Non Proteolytic Aminoacyl Derivatives (NPAD). NPADs were found to be only formed by L-glutamic, lactic and pyroglutamic acids (although in cheese their D-counterparts are abundant) linked to lipohylic amino acids (mostly Phe, Leu, Ile), suggesting a common enzymatic origin, and their amount was found to increase with the ageing time. By using LC/MS technologies, a deep investigation on their origin was undertaken. The cheeses where their amount was found to be higher (up to 50 mg /100 g of cheese) were those with a long ageing time and a consistent presence of lactic acid bacteria. Several strains of lactic acid bacteria, both starters and non starters, isolated from Parmigiano-Reggiano cheese, were found to have the ability to produce gamma-Glu-Phe e Lac-Phe. Experiments with Parmigiano-Reggiano extracts and isotopically labelled precursors indicated the presence in the cheese of an enzymatic activity able to produce these compounds starting from glutamic and lactic acid. Further investigations are now in progress in order to identify and isolate the producing enzyme(s). These compounds demonstrate that the peptidic fraction of Parmigiano-Reggiano is more complex than usually thought, and that enzymatic activities on proteins are not only reponsible for their hydrolysis, but starting from free amino acids can also form new unusual aminoacyl derivatives.

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Keywords: *Peptides; Liquid chromatography; Mass spectrometry; Amino acids;*

P-0614

NEW SPIN PROBES FOR OLIVE OIL CHARACTERIZATION WITH EPR SPECTROSCOPY

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The development of new methodologies utilizing fast and non destructive spectroscopic techniques, such as EPR spectroscopy, in food analysis and characterization has attracted great interest. Despite EPR is a very sensitive and quantifying technique up to date the number of applications developed in Food Science is limited. The current applications are oriented to the determination of the antioxidant activity of foods and the measurement of radical damage after γ-irradiation applied for conservation of food. The absence of naturally spin probes in foods makes difficult the utilization of the EPR spectroscopy, since EPR requires the presence of unpaired electrons. In this study, we develop: (**a**) new probes based on amphiphilic paramagnetic metal species active in the EPR spectroscopy and (**b**) selective oxidative reagents for the endogenous radical generation. The new methods were applied for the analysis of editable oils, in particular for the olive oil. The new methodologies target to utilize EPR towards the determination of olive oil adulteration, and its geographical and botanical discrimination. The main aspects mentioned above have been applied for the authentication of Cypriot olive oils and their classification according to their origin. The probes include amphiphilic molecules incorporating transition metal ion such as V(IV) or Cu(II) as active spin probes, synthesized by the reaction of metal ion salts with the amphiphilic chelators. The oils were titrated with the spin probes, the EPR spectra were recorded at the X-band, and the EPR parameters were determined. In the case of the endogenous radical generation the total antioxidant activity was quantified and the dynamics of radical decay were determined. All the above parameters show that be applied for the discrimination between oils of different botanical origin.

Acknowledgement: *Funding from Research Promotion Foundation and the European Structural Funds program: ΑΝΑΒΑΘΜΙΣΗ/ΠΑΓΙΟ/0308/32*

Keywords: *EPR spectroscopy; Amphiphiles; Radicals; Transition metals;*

P-0615

CHARACTERIZATION OF THE PHENOLIC CONTENT AND AROMA OF THE CYPRIOT WINES FROM INDIGENOUS GRAPE VARIETIES

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An important field of research today is the control of the “redox” status with the properties of food and food components. Natural antioxidants present in the diet increase the resistance towards oxidative damage and they may have a substantial impact on human health. In this aspect, wine has attracted great attention because it contains flavonoids which exhibit antioxidant and free radical scavenging activity in foods. There is accumulating evidence that flavonoids inhibit oxidation of low-density lipoprotein, reduce platelet aggregation, and their consumption always assure a reduced risk of cancer and cardiovascular disease. In Cyprus, indigenous vines varieties are cultivated, survived since the ancient years. Cypriot wines exhibit distinctive flavor and aroma profile, and a rich profile in antioxidants. So far, no records exist in the literature for antioxidant content and the chemical composition of aroma of wines from varieties indigenous to Cyprus. In this study, we demonstrate (**a**) the flavonoids content of and (**b**) their aroma profile of Cypriot wines using chromatographic techniques. The individual polyphenolic constituents were determined by High-Performance-Liquid-Chromatography coupled with diode array detector, utilizing a reverse phase column. Prototypes flavonoids solutions were used as external standards. Volatile compounds were isolated using a Solid-Phase-Micro-Extraction Head space technique and then separated and semi-quantified on a polar capillary column using a Gas-Chromatograph with a Mass Spectrometer detector. Identification of the volatiles was performed by using standards, the Kovat’s Index, and the MS library, while quantification was done using an internal standard. Determination of the flavonoids composition and the chemical composition of volatiles were performed for the indigenous and European varieties cultivated in Cyprus. The results showed that the Cypriot wines derived from the indigenous varieties have a rich aroma and high content of antioxidant compounds.

Acknowledgement: *Funding from Research Promotion Foundation and the European Structural Funds, program: ΑΝΑΒΑΘΜΙ∑Η/ΠΑΓΙΟ/0308/32*

Keywords: *Antioxidants; Aromaticity; Liquid chromatography; Gas chromatography; Mass spectrometry;*

P-0616

CHEMICAL STRUCTURE AND MEMBRANE INTERACTIVITY RELATIONSHIP OF NUTRACEUTICAL FLAVONOIDS IN FOODS AND BEVERAGES: THEIR ANTIPROLIFERATIVE EFFECTS ASSOCIATED WITH THE CHARACTERIZED RELATIONSHIP

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Introduction: Flavonoids are referred to as nutraceuticals which provide plant-derived foods and beverages with disease preventive and therapeutic potentials. However, beneficial effects are significantly influenced by their chemical structures. Apart from acting on proteinous target enzymes and receptors, flavonoids also mechanistically interact with lipid bilayer membranes. We characterized the structure and membrane interactivity relationship of nutraceutical flavonoids, and verified their antiproliferative effects associated with the relationship.

Methods: Biomimetic membranes were prepared with phospholipids and cholesterol, and they were reacted with 32 structurally-relating flavonoids (flavones, flavonols, flavanones, flavanonols, anthocyanidins, flavanols and isoflavones) of 0.1–10 μM. The membrane interactivities of flavonoids were compared using the potencies to modify membrane fluidity by measuring fluorescence polarization with different probes. Their antiproliferative effects were determined by assaying the growth inhibition of mouse myeloma cells.

Results: Flavonoids structure-dependently acted on the deeper hydrophobic regions of lipid bilayers to decrease membrane fluidity. The characterized relationship between structure and membrane interactivity indicated that 3-hydroxylation of the C ring, a double bond between 2-carbon and 3-carbon of the C ring, 3',4'-dihydroxylation of or no substituents on the B ring, and 5,7-dihydroxylation of the A ring are important for flavonoids to show greater membrane interactions. As the basic structure, flavonoids were far preferable to isoflavonoids. Aglycones were much more effective in rigidifying biomimetic membranes than glycosides. Quercetin, galangin, cyanidin and (–)-epigallocatechin gallate, meeting these structural requirements, inhibited the growth of tumor cells at 10–100 μM. These antiproliferative flavonoids decreased the fluidity of tumor cell membranes with the potency correlating to the relative cell growth-inhibitory activity.

Conclusion: Membrane-interacting anti-tumor flavonoids are contributable to the medical health benefits of plant-derived foods and beverages. However, attention should be paid to the possibility that nutraceutical flavonoids may exert adverse effects by interacting with membrane-active drugs in the combination therapy.

Keywords: *Structure-activity relationships; Membranes; Lipids; Natural products; Antiproliferation;*

P-0617

DETERMINATION OF STILBENES AND 2,4,6-TRIHYDROXYPHENANTHRENE-2-O-GLUCOSIDE IN GRAPEVINE LEAVES INFECTED BY PLASMOPARA VITICOLA

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Plasmopara viticola stimulates the synthesis of stilbenes and 2,4,6-trihydroxyphenanthrene-2- O-glucoside in grapevine leaves (Tríska et al. 2012), where 2,4,6-trihydroxyphenanthrene-2-O-glucoside arises from *cis*-piceid by cyclization. Infected leaves of Pinot blanc, Pinot gris and Cabernet sauvignon were lyophilized, grounded and than extracted with 70% methanol. Extracts were analysed by reverse phase liquid chromatography using Hewlett Packard instrument and columnn Phenomenex Luna C18 (2) in gradient acetonitril-water-phosphoric acid. Compounds were detected by DAD and FLD detectors (Agilent). Phenanthrene derivative was confirmed also LC/MS measurements. LC/MS were carried out using the Thermo Accela, LCQ Fleet ion trap LC-MS instrument and APCI ionization technique in the positive mode.

Values of *trans*-resveratrol were in ranges of 7-17mg/kg, *trans*-pterostilbene 0.3-1 mg/kg, *cis*-piceid 54-108 mg/kg and 2,4,6-trihydroxyphenanthrene-2- O-glucoside 34-60 mg/kg.

Acknowledgements: *This study was funded by the Grant Agency of the Czech Republic, grant number 525/09/0365, and by CzechGlobe - Centre for Global Climate Change Impacts Studies, Reg. No. CZ.1.05/1.1.00/02.0073.*

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Keywords: *Phytochemistry; UV/Vis spectroscopy; Mass spectroscopy; Biological activity;*

P-0618

LC-ESI-MS/MS STUDY OF CHLORAMPHENICOL DISTRIBUTION ON CHEESE MAKING

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Chloramphenicol (CAP) is effective antibiotic, which use is prohibited in food-producing animals. EU defined MRPL for CAP in food of animal origin - 0.3 µg/kg. Chloramphenicol control in raw milk is obligatory for cheesemakers. Since on manufacturing CAP may concentrate in cheese, then there is possibility to obtain contaminated product from allowable milk. Therefore, we developed LC-ESI-MS/MS method for CAP residues determination in cheese. Sample preparation was as follows: CAP extraction with ethyl acetate from grated cheese, evaporation, defatting and SPE clean-up. HPLC conditions: C_{18} column; mobile phase - water - methanol. Analyte was quantified by negative ion mode LC-ESI-MS/MS (MRM of m/z 321≥152 and 321≥257). LOQ = 0.02 µg/kg.

Since cheese sample matrix is complex, then minced cheese fortifying with internal or external CAP standard may not represent adequate recovery of analyte, present in initial milk. Therefore, we prepared cheese reference matrix to estimate the elaborated method's recovery. Cheese was made in laboratory according to general procedure using blank cow's milk, divided into two equal parts, one of which was spiked with 0.5 µg/kg CAP. Milk, whey, cheese and salt solution were sampled during cheese preparation and ripening.

It was ascertained, that on cheese making 78% of chloramphenicol, added into initial milk, accumulates in whey, while 20% in cheese and 2% in salt solution. If milk contains 0.5 µg/kg CAP, then CAP concentration in cheese and whey will equal 0.8 and 0.45 µg/kg, respectively. Hence, irregular chloramphenicol distribution occurs in main and by-products, therewith CAP concentration in cheese is 1.5-2-times higher than in utilized milk. Thus, even when making cheese from milk containing CAP level lower than MRPL, there is a possibility to obtain contaminated cheese.

It was established, that chloramphenicol recovery from cheese with developed method is ~90%. Also, techniques for CAP determination in whey and salt solution were elaborated.

Keywords: *Mass spectrometry; Liquid chromatography; Antibiotics;*

P-0619

LOW TEMPERATURE OF THE METHANE COUPLING WITH UV-ACTIVATION IN THE MEMBRANE REACTOR

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The basic methods to produce hydrocarbon C_2 and above from methane is a thermal activation of the CH_4 molecules that breaks C-H bonds that often caused an uncontrolled breakup of these bonds with free carbon formation. To use the ultraviolet activation allows conducting the process under low temperature, but because of the reaction reversibility the methane conversion remains low. The membrane reactor makes to shift equilibrium possible by hydrogen removing from the reaction space and therefore to increase the methane conversion.

The experiments were provided under atmospheric pressure of the pure methane (99.99%) in the temperature interval 200–270°C with a mercury lamp. The membranes in the form of Pd-Ru alloy tubes (diameter 1 mm, wall thickness 50 mkm, 1 or 1.7 m lengths) were placed inside the quartz glass reactor filled with CH_4. Any gas flow inside the tube allowed moving off the hydrogen that penetrated through the membrane from the reaction space outside this tube. The mane products analysed by GC were propane and ethane with small quantity of the ethylene.

The methane conversion with 1 m tube at 215°C was four times higher (5.2 %) when hydrogen was removed through a membrane than without hydrogen removing off at the same temperature. The highest obtained conversion was 14.3 % at 265°C with hydrogen removing off from the reaction space.

Probable products formation mechanism

$$CH_4 \text{ -> } CH_3\cdot + H\cdot$$

$$CH_4 \text{ -> } CH_2\text{:} + H_2$$

$$2CH_3\cdot \text{ -> } CH_3\text{-}CH_3$$

$$CH_2\text{:} + CH_3\text{-}CH_3 \text{ -> } CH_3\text{-}CH_2\text{-}CH_3$$

$$2CH_2\text{:} \text{ -> } CH_2{=}CH_2$$

$$2H\cdot \text{ -> } H_2$$

The methane molecules' activation by the UV-radiation allows providing their coupling under comparatively low temperature that reduces power inputs and a deep dehydrogenation with free carbon formation. To use a palladium alloy membrane reactor allows increasing the methane conversion due to hydrogen removing from the reaction space.

P-0620

KINETICS OF DYE LOADING PROCESS IN DYE SENSITIZED SOLAR CELLS BY MEANS OF REAL TIME DYE UPTAKE MONITORING

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Since their set up, dye sensitized solar cells (DSCs) have attracted a remarkable interest as promising alternative devices to silicon-based photovoltaic technology[1]. However, device fabrication is an “artisanal” multi-step procedure still lacking of rationalisation. Dyeing process holds a relevant impact on both cell performances and scale-up perspective[2]. Indeed, DSCs are currently sensitized by means of a static impregnation process lasting about 20 hours, which would be time expensive in view of an industrial scale up.

Herein we present a study on the real-time monitoring of dye loading process by means of UV-vis spectrophotometry allowing to rationalize the kinetics of dye uptake in both static and dynamic condition for the classical Ru-based N719 and N3 dyes at different concentrations on nanoparticulate TiO2 photoanode[3].

Dynamic dye uptake was found to follow a two-step process, composed of a first faster contribution indicating a pseudo-first order kinetics (tens to hundreds of seconds) followed by a slower absorption according to a zero-order kinetics (hours).

The choice between dynamic and static sensitization approaches turned out to heavily affect the final dye loading. Although the same mechanism was operating in both cases, dynamic uptake was found to provide for a lower dye loading, which is reflected in poorer DSC performances (a decrease of about 20% was found as for photoconversion efficiency).

Although a prudential attitude should be adopted when comparing the two approaches, dynamic sensitization could be a powerful tool towards a reproducible and fully controllable fabrication of DSCs.

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Keywords: *dye sensitized solar cells; dye loading kinetics;*

P-0621

EFFECTS OF CR_2O_3 MODIFICATION ON THE PERFORMANCE OF SNO_2 ELECTRODE IN DYE-SENSITIZED SOLAR CELLS

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We demonstrate that Cr_2O_3, a visible absorbing insulator, can be used as an efficient blocking layer material for the anode of dye-sensitized solar cells (DSSCs). We prepared SnO_2 electrodes surface-modified with Cr_2O_3 with various Cr/Sn ratios and studied the effect of the modification on the performance of DSSCs. DSSCs with Cr/Sn ratios 0.02, 0.05, and 0.10 showed increased overall photon-to-electricity conversion efficiency from that of pure SnO_2. When Cr/Sn ratio was 0.02, 55%-improved overall conversion efficiency was measured and the ratio 0.05, 40% compared with pure SnO_2 cell. The physical properties of Cr_2O_3-modified SnO_2 were studied by X-ray diffraction, transmission electron microscopy, N_2 adsorption studies and UV-Vis diffuse reflectance spectroscopy. The electrochemical properties of Cr_2O_3-modified SnO_2 were studied by Mott-Schottky plots and electrochemical impedance spectroscopy.

Keywords: *Dye-sensitized solar cell; blocking layer;*

P-0622

ABSORPTION OF CO_2 INTO AQUEOUS POTASSIUM SALT SOLUTIONS OF AMINO ACIDS

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Since the industrial revolution, fossil fuel consumption has drastically increased. Carbon dioxide discharged from combustion processes is now believed responsible for global warming and an increase in the earth's average temperature. The development of CO_2capture technologies is critical for reducing greenhouse gases and coping with the climate change problem at its root. Monoethanolamine (MEA) is the leading alkanolamine absorbent. Although it features a fast absorption rate and a high alkalinity, it has the drawbacks of loss of absorbent due to degradation and corrosion of the equipment as well as the high amounts of energy required for absorbent regeneration. To solve these problems, the absorption of CO_2 using an amino acid salt solution as an alternative absorbent was studied. In this study, the CO_2 absorption capacity and absorption heat of the aqueous potassium salts of L-alanine and L-proline were investigated using a semi-batch absorption system and a differential reaction calorimeter (DRC). The speciation in the CO_2-loaded absorbents was investigated using NMR spectroscopy. The results were compared with primary amine, MEA and secondary amine, diethanolamine (DEA). The CO_2 loading capacities were found to be 0.50 and 0.68 mol CO_2/mol solute for aqueous MEA and potassium salt of L-alanine at 298 K, respectively. The CO_2 absorption heats of the potassium salt of L-alanine and potassium salt of L-proline were lower than those of MEA. The absorption heats were found to be 81.77, 67.06, 53.26 and 90.20 kJ/mol-CO_2 for aqueous MEA DEA, potassium salt of L-alanine, and potassium salt of L-proline, respectively. It was found that the potassium salt of L-alanine had an excellent for CO_2 capture. Therefore, the potassium salts of L-alanine and L-proline are deemed to be the potential CO_2 absorbent to replace the existing amines.

Keywords: *CO_2 Capture; Amino Acids; Amine;*

P-0623

WATER OXIDATION BY SINGLE-SITE RUTHENIUM COMPLEXES – USING LIGANDS AS REDOX AND PROTON TRANSFER MEDIATORS

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The splitting of water into molecular oxygen and hydrogen gas is an attractive option for the production of sustainable energy, where mastering the process of oxidizing water is the key step for the utilization of this potential. The possibilities are enormous, where the later can be used as a fuel, stored for future demands, or even to be used for the production of more complex fuels and chemicals.

A serious problem is that most of the catalysts developed so far require a powerful sacrificial oxidant, i.e. Ce^{IV}, to be able to oxidize water. In a sustainable system, the oxidant needs to be a light-absorbing component, a photosensitizer, which can be regenerated. A major obstacle in light-driven water oxidation is frequently the mismatch between the relatively high redox potential at which a catalyst assumes its active state and the lower potential attainable with a photosensitizer.

Comprising a redox and proton transfer mediator motif into the WOC would facilitate the simultaneous transfer of electrons and protons, thus avoiding high-energy intermediates and give access to new reaction pathways. In order to both decrease the redox potentials and permit coupled proton-electron transfer, imidazole and carboxylate were introduced as mediators into the ligands. Therefore the meridionally coordinating benzimidazole based ligands **1** and **2** and their related single-site ruthenium complexes **3** and**4** were synthesized. Indeed, by introducing the redox and proton transfer mediator motif (imidazole) the WOCs were able to catalyze water oxidation, under neutral conditions, both by pre-generated and photogenerated $[Ru(bpy)_3]^{3+}$.

Keywords: *Water splitting; Sustainable chemistry; Ruthenium; Photochemistry; Electrochemistry;*

P-0624

PHOTOCHEMICAL WATER OXIDATION – INSPIRED BY NATURE

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The direct conversion of solar energy into energy by the splitting of water into molecular oxygen and hydrogen gas, or even more complex fuels holds high potential in realizing a sustainable energy production for our future demands. Water oxidation is currently restricting the development of solar-energy devices and is considered to be essential to fully utilize this potential.

The development of environmentally benign, abundant and thus inexpensive first row transition metal catalysts is of utmost importance for the incorporation into molecular light-harvesting devices on a large scale. To date, there are only a handful of homogeneous water oxidation catalysts which are capable of managing the difficult task of oxidizing water.

Herein we report that the dinuclear manganese complex **1** is capable of mediating the four electron oxidation of water, both by using a chemical oxidant and photochemically. Complex **1** is based upon a bioinspired ligand containing imidazole and carboxylate functionalities, which are both important components in the natural system. To the best of our knowledge this is the first example of a homogeneous manganese based water oxidation catalyst.

Keywords: *Water splitting; Manganese; Photochemistry; Sustainable chemistry;*

P-0625

CLYSTAL GROWTH OF SEMICLATHRATE HYDRATE FORMED WITH TETRA-N-BUTYL AMMONIUM BROMIDE AND CARBON DIOXIDE

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This paper reports a visual crystal growth study concerning the separation of carbon dioxide utilizing formation and dissociation of clathrate hydrate. The obstacle to realize this hydrate technology is high pressure required for the hydrate formation. The high equilibrium pressure of CO_2 hydrate may be moderated with the addition of a second guest substance such as tetra-n-butyl ammonium bromide (TBAB).Visual observations were carried out on the formation and growth of semiclathrate hydrate crystals in the system of CO_2 + TBAB + water. The experimental thermodynamic conditions are (**i**) at pressure of 2.3 and 3.4 MPa and temperature range of 286 to 290 K for $w_{TBAB} = 0.40$, (**ii**) at pressure of 2.3 and 3.4 MPa and in the temperature range of 282 to 288 K at $w_{TBAB} = 0.10$ where w_{TBAB} denotes the mass fraction of TBAB in the aqueous liquid. A hydrate crystal first formed in aqueous liquid or to intervene between the gas and aqueous liquid phases. Then hydrate crystals grew into aqueous liquid phase. The morphology of hydrate crystals grown in aqueous liquid varied distinctly depending on the system subcooling ΔT_{sub}. ($\Delta T_{sub} \Xi T_{eq} - T_{ex}$, where T_{eq} is the equilibrium temperature of the hydrate at each mass fraction and T_{ex} is the system temperature).When ΔT_{sub} is smaller than ~ 2.0 K, hydrate crystals with planar morphology were observed. At the range of ~3.1 K > ΔT_{sub} > ~2.0 K, the planar crystals were replaced by columnar and sword shaped crystals. At ΔT_{sub} > ~3.1 K, hydrate crystals with needle morphology were observed. Pressure dependence of hydrate crystal morphology was not observed. The size of the individual hydrate crystals decreased with increasing ΔT_{sub}. We also observed the crystals floating in aqueous liquid at ΔT_{sub} > ~3.1 K

Keywords: *Clathrates; Hydrates; Crystal engineering; Crystal growth; Carbon dioxide fixation;*

P-0626

PT/N-CODOPED TIO$_2$ NANOTUBE ARRAYS FOR PHOTOCATALYTIC HYDROGEN EVOLUTION

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In this study, The Pt/N-codoped TiO$_2$ composites were synthesized using TiO$_2$ nanotube arrays as a support. The TiO$_2$ nanotube arrays were electrochemically fabricated using 20 × 20mm titanium and Pt foils as the anode and cathode, respectively. In addition, Pt ions and ammonia were loaded onto the TiO$_2$ nanotube arrays to from Pt/N-codoped TiO$_2$ composites for enhanced photocatalytic reaction. The microstructures of TiO$_2$ nanotubes including morphology, optical property, and crystallinity were determined. In addition, effect of operational parameters including catalyst loading, solution pH, and anneal temperature on the production of hydrogen gas were examined and optimized. The TiO$_2$ nanotubes have several nm in diameter and tens of μm in length after 5 h of anodization. The TEM images showed that Pt nanoparticles were well-dispersed on the surface of TiO$_2$ nanotubes with diameter of 5-10 nm. In addition, TiO$_2$ and Pt/N-codoped TiO$_2$ nanotube arrays were used for photocatalytic hydrogen generation. The hydrogen production rate from water by Pt/N-codoped TiO$_2$ nanotube arrays was higher than that of pure TiO$_2$ nanotube arrays. Results show that photocatalyst with optimal operational conditions could lead to enhanced hydrogen production rate.

Keywords: *TiO2 nanotube arrays; Codoping; Photocatalytic Hydrogen Evolution;*

P-0627

IDENTIFICATION OF GASOLINE ADULTERATION BY THE ADDITION OF SOLVENTS, TAGGED WITH TRACERS, IN A PROGRAM CREATED BY THE BRAZILIAN GOVERNMENT

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Gasoline adulteration, through the addition of unauthorised solvents or kerosene, is a serious problem facing many national governments and producers today. The principal of tracer technology is that a material not found naturally within the fuel is added at ultra low levels to potential adulterants. An analysis of suspect fuel showing the tracer confirms adulteration. In many instances where a tracer material is added to potential adulterants, there is an incentive for the illicit removal of the taggant, often termed ‘laundering’. Therefore it is essential that the tracer is highly resistant to laundering by the methods likely to be used by those adulterating the gasoline. This system is adopted in Brazil, where the solvents are tagged to prevent and detect the adulteration of gasoline by the addition of these products. The Brazilian Program was a pioneer worldwide, since we decided to tag the adulterant instead of the gasoline. The chemical tracer used in the Program is detected by Gas Chromatography/Mass Spectrometry with NCI source employing suitable detection methods. The method allows the detection of the tracer at very low concentration (ppb), providing great reliability in identifying gasoline adulteration by the addition of solvents, even at very low concentrations. This paper describes the application of the GC/MS based system, and demonstrates why it is the analytical technique of choice for measuring ‘launder’ resistant taggants. It also highlights the positive results achieved in the last 10 years during use in the Brazilian Program to counter the adulteration of gasoline by the addition of solvents.

Keywords: *gasoline adulteration; identifying tracers in gasoline by GC/MS; energy; fuels; brazilian program;*

P-0628

STUDY OF CYANO-SUBSTITUTED HYDRAZINIUM SALTS FOR ENERGETIC APPLICATIONS

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1,1-Dimethylhydrazine can be readily alkylated with bromoacetonitrile to form 1-cyanomethyl-1,1-dimethylhydrazinium bromide ($[(CH_3)_2N(CH_2CN)NH_2]Br$, **1**). Metathesis of the bromide anion in **1** with an energetic anion transfer reagent lead to the formation of a new family of salts based on the $[(CH_3)_2N(CH_2CN)NH_2]^+$ cation and nitrate (**2**), perchlorate (**3**), azide (**4**), 5-aminotetrazolate ($[H_2N–CN_4]^–$, **5**), 5,5'-azobistetrazolate ($[N_4C–N=N–CN_4]^{2–}$, **7**) and picrate (**8**) anions. The new materials were characterized by elemental analysis, mass spectrometry and (multinuclear) NMR and vibrational (infrared and Raman) spectroscopies. Additionally, the molecular structure of the $[(CH_3)_2N(CH_2CN)NH_2]^+$ cation in compounds **1**, **3** and **8** and that of sodium 5,5'-azobistetrazolate octahydrate ($NaZT*8H_2O$) were solved by X-ray diffraction techniques. The hydrogen-bonding networks found in the structure of salts **1**, **3**, **8** and $NaZT*8H_2O$ is described using graph-set analysis. The melting and decomposition points of the new compounds was determined by differential scanning calorimetry and all materials were submitted to standard tests to gain insight into their sensitivity towards impact, friction and electrostatics. Furthermore, we estimated some performance parameters of interest and we predicted the decomposition gases formed upon decomposition of the materials in this study and of their mixtures with an oxidizer. The interesting thermal, sensitivity and performance properties of some of the compounds make them attractive candidates towards a prospective energetic application.

Keywords: *Nitrogen; Ion exchange; NMR spectroscopy; Quantum Chemistry; X-ray diffraction;*

P-0629

CO_2 ABSORPTION CHARACTERISTICS OF AQUEOUS AMINO SILANE

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There are many ways to reduce CO_2 emission such as pre- and post-combustion capture technologies these days. Also lots of studies have been conducted about this area. One of them is absorbent for CO_2 capture. Moreover, the study on the applications of absorbents for pilot plant is performed using absorbent such as commercial MEA. In this study, we investigated the possibility of amino-silane series as an absorbent for CO_2 absorption. CO_2 absorption capacity and characteristics of amino-silane series were examined at the following conditions; temperatures (30, 50, 70?), pressure (1~30 bar). In addition, we investigated CO_2 absorption capacity and characteristics of amino-silane series with different ratios of amino-silane to distilled water. Based on the results, we compared amino-silane with MEA. In order to evaluate CO_2 absorption capacity and characteristics, we prepared equipments at constant temperature and pressure conditions. We removed water and other impurity gases in the equipment cells before experiments. High purity CO_2 gas (99.9%, Dukyang energen gas corporation, Korea) was used for experiments. As the experiment was performed, CO_2 absorption into absorbent was started and maintained for enough time until equilibrium condition between absorbent and CO_2. At that time, we calculated CO_2 absorption rate and absorption amount of the amino silane series. As the result of the experiments, CO_2 absorption capacity and absorption rate increased together with increasing the amount of amino silane in the mixture. We observed that all experiments were reached at equilibrium within 3 hr, although each equilibrium times are a little different. In this work, we confirmed CO_2 absorption capacity and characteristics of amino silane series.

Keywords: *carbon dioxide; capture; amino silane; greenhouse gas; global warming;*

P-0630

GLYCEROL COMPOUND USED AS A GREEN COMPONENT FOR DIESEL FUEL

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Biodiesel is a good alternative for diesel fuel. Each tonne of produced biodiesel, generates more than 100 kg of crude glycerine which can be converted into useful products. An important direction for crude glycerine valorization is transformation into glycerol acetals/ketals that can be used as additives and/or components of classic diesel fuels.

This paper presents the synthesis of 4-methylpentan-2-one glycerol ketal obtained from condensation of 4-methylpentan-2-one with glycerol, catalyzed by a solid superacid. The obtained glycerol compound was tested as diesel fuel component, focusing our interest in cold flow properties, viscosity and flash point.

The catalytic ketalization of glycerol was made in presence of SO_4^{2-}/TiO_2-ZrO_2. The catalyst was prepared by coprecipitation followed by vacuum sonicated impregnation and characterized by X-ray diffraction, thermogravimetric analysis, FT-IR spectroscopy and elemental analysis. To determinate the optimal parameters, five impact factors were investigated in the experiments: molar ratio glycerol/4-methylpentan-2-one, catalyst calcination temperature, reaction time, catalyst amount and molar ratio of Ti/Zr. Synthesized ketal was analyzed by GC–MS/MS. The experimental results shows the maximum yield in 4-methylpentan-2-one glycerol ketal of 92% was reached at molar ratio ketone to glycerol 1.1:1, mass ratio of the catalyst 1.5 wt % with respect to glycerol, reaction time 6.5 h, catalyst calcination temperature 550°C for 3 h and molar ratio Ti/Zr = 4:1.

The influence of viscosity, pour point and flash point on the quality parameters of diesel fuel blends with 2, 5, 7 and 10% of oxygenated compound were studied. The data obtained shows that of 4-methylpentan-2-one glycerol ketal slightly changes the flash point (from 61.1 to 62.1°C), but improves the pour point (from -13 to -23°C) and viscosity (from 2.7 to 2.59 mm^2/s).

Keywords: *glycerol; solid superacid; ketal; diesel component; 4-methylpentan-2-one;*

P-0631

HYDROGEN PERMEATION PROPERTIES OF VANADIUM-BORON ALLOY MEMBRANES FOR PRE-COMBUSTION CARBON DIOXIDE CAPTURE PROCESS

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Novel membranes composed of the vanadium-boron alloys have been developed for the hydrogen separation in pre-combustion CO_2 capture process. Group 5A metals, such as vanadium are promising candidates for hydrogen permeation alloys because of their high hydrogen permeability values, however these metals alloys suffer from severe hydrogen embrittlement. In this work, a small amount of boron was added into vanadium base metal to enhance the stability of membrane during hydrogen separation. The hydrogen permeation experiments have been conducted to investigate the hydrogen transport property through the Pd-coated vanadium-boron alloy membrane under simulated gas feeding condition such as pure hydrogen and hydrogen-carbon dioxide gas mixture. Pressure was controlled with back pressure regulator in the region of 1.0~3.0 bar at 400 °C. Hydrogen fluxes agreed with Sievert's law irrespective of feeding condition. The maximum hydrogen flux of a 0.5 mm thick membrane was 48.5 ml/min•cm^2 at 400 °C under pure hydrogen feeding condition.

Keywords: *vanadium; boron; metal alloy membrane; hydrogen separation; carbon dioxide capture;*

P-0632

EXTRACTION OF LIPIDS FROM ALGAE WITH SWITCHABLE SOLVENTS

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Microalgae represent a very promising source of third generation biofuels. Benefits rising from the utilisation of aquatic over terrestrial biomasses are varied, however lipid extraction is currently a critical step in the industrial development of these biofuels. Here we propose a new green procedure based on switchable-polarity solvents (SPS) for the extraction of algal lipids from both dried samples and concentrated cultures. SPS are capable to turn from a non-ionic form, suitable for lipid extraction, to an ionic liquid, suitable for a recovery step, by simply bubbling CO_2, and to be reconverted in the non-ionic form by bubbling N_2 or by heating[1]. We present the results obtained with different classes of SPS: **i**) one based on 1,8-diazabicyclo-[5.4.0]-undec-7-ene (DBU) and alcohols (ROH), switchable in alkylcarbonate salts; **ii**) the second based on alkyl amines (as *N,N*-dimethylcyclohexylamine, DMCHA) and water, switchable in hydrogencarbonate salts.

The SPS were tested for the extraction of lipids from freeze-dried samples and directly from aqueous growth medium of several microalgae, as *Botryococcus braunii,* rich in unsaturated hydrocarbons[2], and other freshwater and marine species (e.g. *Chlorella sp., Nannochloropsis sp.* and *Desmodesmus sp.*) and compared with the efficiency of traditional organic solvents (e.g. *n*-hexane and chloroform/methanol mixture).

The use of a green technology suitable for extracting lipids from both dried microalgal biomass and directly from aqueous growth medium is an important issue considering that the harvest and the dewatering of algal biomass have a large impact on overall costs and energy balance. Besides the efficiency in lipid extraction, SPS have the great advantage to be recyclable non-volatile/non-inflammable systems, therefore suitable for non-hazardous small plants for biofuel production located nearby algal cultivation sites.

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Keywords: *algae; switchable solvents; biofuels;*

P-0633

COMPARISON OF CHEMICAL AVAILABILITY, POLLUTANT AND CO_2 EMISSIONS FROM HYDROGEN, ETHANOL AND NATURAL GAS AS ENGINE FUELS

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The chemical availability of green fuels hydrogen and ethanol has been calculated and compared with common engine fossil fuels gasoline and natural gas. Other parameters evaluated were the concentrations of carbon monoxide (CO), nitric oxide (NO) and carbon dioxide (CO_2) as combustion products. The analysis has been carried out through an engine cycle simulation model developed using Engineering Equation Solver software. The results show that hydrogen present superior exergetic efficiency in comparison with gasoline and natural gas. Ethanol produced lower exergetic efficiency than the fossil fuels. CO and CO_2 concentrations are significantly reduced with the use of the green fuels, while NO concentration showed less accentuated reduction.

Keywords: *Hydrogen; Biomass; Energy Conversion; Renewable Resources; Thermochemistry;*

P-0634

A SIMPLE DIDACTIC MODEL OF MHD POWER GENERATOR FOR THE STUDENTS LABORATORY

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MHD (magnetohydrodynamic) generator is a heat engine that operates by passing a high velocity jet of partially ionized gas through a magnetic field to produce electricity. In effect, the solid rotor of conventional generator replaced with a plasma “rotor”.

The advantages of such system are obvious. The plasma rotor can not melt in a high temperatures, so higher input temperatures and higher power producing efficiencies are possible. This rotor has little mechanical inertia, so the start-up time can be quite short.

In order to achieve high efficiency of the MHD generator, the electrical conductivity of the plasma jet must be as high as possible. In my project, the flame is seeded with easily-ionized potassium (EI = 4,34 eV), and is highly conducting even at relatively low temperatures. In addition, thermal ionization of the exhaust gas takes place.

A simple demonstration model MHD generator based on a small solid-fuel rocket motor (with black powder propellant) as a power source. The motor is exhausting between the poles of a two neodymium magnets. Steel electrodes placed at the edges of the gas jet detect the generated voltage for display on a digital multimeter (voltmeter). A rocket motor provides about five seconds of running time.

Both the open-circuit voltage (several volts) and the short-circuit current (several miliamperes) can be calculated, giving students an excellent insight into the properties of this power system.

In this study, basic assumptions and requirements to be taken into account in designing and building a model MHD generator are presented. In addition, modelling of a composite propellant including potassium is described. The parameters such as ionization ratio, electrical conductivity, chemical composition of exhaust gas and open-circuit voltage were also evaluated.

Keywords: *energy conversion; environmental chemistry; plasma chemistry; thermodynamics;*

P-0635

THE DIRECT SYNTHESIS OF HYDROGEN PEROXIDE BASED ON MICROREACTOR TECHNOLOGY

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We successfully conducted the direct syntheisis of hydrogen peroxide using applying microreactor technology to produce aqueous solution of 10 wt%, under rather ambient condition (1 MPa, no cooling effort). The microreactor design was mandatory to proceed the reaction safely and efficiently. For the direct synthesis reaction is three phase reaction (gas, liquid and solid i.e. catalyst), proper distribution of both gas and liquid phase over catalyst is mandatory, which has been realized by our reactor design. Heat removal nature also worked favorable to maintain the reaction not only operatable but also productive for hydrogen peroxide. Also, proper choice of the catalyst promoted the concentration of hydrogen peroxide we provided. Our kinetics analysis indicated that hydrogen and oxygen reaction is a cascade reaction, whose primary product was hydrogen peroxide and water was subsequently produced. The second step was unfavorable to achieve high concentration of hydrogen peroxide. Details of the kinetics analysis will be presented on site.

Keywords: *hydrogen peroxide; direct synthesis;*

P-0636

SYNTESIS OF BIOLOGYCAL ACTIVE COMPOUNDS FROM VEGETABLE RAW MATERIALS HAS ANTIOXIDANT PROPERTIES

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The Republic of Kazakhstan has little of its pharmaceutical industry. Almost 90% of medicines are imported from far and near abroad, on a national scale spent huge sums in foreign currency. Drugs made from plant material, are especially effective in the treatment of diseases caused by unfavorable environmental conditions (Baikonur Spaceport, the Semipalatinsk nuclear test site) and the high background radiation do not cause side effects when they are used and are not toxic than drugs obtained by synthesis. In Kazakhstan, there are over 20,000 species of plants, 6,000 of them contain biologically active substances. Of the six thousand six hundred species can be used as an intermediate product for the production of drugs, and from more than 500 species can be ready to receive drugs. But the existing technology of medicines are very complicated and many-stage, energy-intensive and costly process. In addition, the purity of the products is poor, so they are not competitive on the world market. In Shymkent chemical-pharmaceutical plant from plant material obtained by extraction of drugs: morphine, codeine, papaverine, etc., and related alkaloids are in the blade, as some of them exhibit the toxicity, while others are ineffective, and some do not possess physiological activity. But the structure of these alkaloids can get from them is already known or new biologically active compounds by modifying their structure, by introducing new functional groups-OH, $-OCH_3$, $-OC_2H_5$, $-NO_2$, etc. These biologically active agents are effective in the treatment of cancer and have antioxidant properties. To determine the molecular formula of compound chromatographically pure samples of the final products were subjected to qualitative and quantitative elemental analysis for carbon, hydrogen, nitrogen, bromine, according to the method. Belonging to a class of products com tions revealed the following way. Quantitative analysis on the methoxy group was carried out by the modified method Tseyzelya-Fibeka.

Keywords: *Alkaloids; Biological activity; Antioxidants; Electrochemistry; Biomass;*

P-0637

PHOTOINDUCED DECARBOXYLATION OF AMINO ACIDS BEARING FURAN MOIETY

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Photochemistry and photocatalysis have found wide applications in organic chemistry. Light is an abundant and renewable energy source for new reactions and chemical transformations under mild and green conditions.[1] Okada and coworkers demonstrated redox photodecarboxylation of phthalimide esters using visible light.[2]

We applied Okada's approach to a sustainable chemistry using furans and amino acids as renewable resources. As a model compound we synthesized N-Furoyl-β-amino acid activated by a phthalimide moiety. Visible light (455 nm LED) mediated and $[Ir(ppy)_2(dtbbpy)]PF_6$ catalyzed decarboxylation leads to a primary alkyl radical. This radical undergoes an 5-exo-trig intramolecular cyclisation to an allylic cation and the spirolactol 7-tert-butyl-2-hydroxy-1-oxa-7-azaspiro[4.4]non-3-en-6-one. The reaction scope was demonstrated on 10 examples.

An acid catalyzed vinylogus semi-pinacol rearrangement into Furo[2,3-c]pyridinone was discovered for the photoreaction product. The plausible mechanism includes as an intermediate the same allylic cation which was proposed for phototransformation. Thus a cascade process could be developed.

As an application of this chemistry we envisage a total synthesis of (-)-Stemoamide. Results may be expected in due course.

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Keywords: *Photocatalysis; Decarboxylation; Cyclisation;*

P-0638

MEMBRANE INTERACTIONS OF IONIC LIQUIDS

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Ionic liquids (ILs) are organic salts with relatively low melting points and unique properties dependent upon the constituent cation and anion which can be separately modified. ILs have attracted great interest as an environmentally-benign source for alternative solvents, however, their broad solvation properties and their high solubility in water present health risks, since many ILs have proven to be cytotoxic.

The mechanisms of ILs toxicity, however, are not well understood. Most studies have correlated the lipophilicity of ILs ion-pairs with their biological effects[1], suggesting that disruption of the plasma membrane plays a major role in ILs toxicity[2]. We present here a comprehensive biophysical and microscopy study of membrane interactions of a series of ILs containing imidazolium and pyrrolidinium head groups with long, short and diethoxylated alkyl chain. The bio-analytical tests include vesicles dye release assay, confocal fluorescence microscopy, FRET analysis with small unilamellar vesicles, and lipid/polydiacetylene assay.

Results point to group the compounds tested according to bilayer interactions. Specifically, IL with long alkyl chain exhibited the most pronounced binding and disruption effect of membrane bilayers, ILs with short alkyl chains also appeared fairly membrane-active whereas imidazolium oxygenated ILs featured the lowest bilayer activity among the compounds studied. This trend is in general agreement with previous studies on ILs cytotoxicity[3] and will be helpful for the design of new classes of ILs exhibiting benign environment profiles.

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Keywords: *Ionic Liquids; membranes; cytotoxicity;*

P-0639

ELECTROCHEMICAL OXIDATION OF METHANOL BY CARBON SUPPORTED PLATINUM NANOPARTICLES PREPARED BY NEW SURFACTANTS

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In this study, platinum nanoparticle catalysts have been prepared using $PtCl_4$ as starting material, and 1-hexylamine, methylhexylamine and dimethylhexylamine as surfactants. All of those surfactants were used for the first time to see the effect of surfactants on the size of platinum nanoparticles and catalytic performances towards methanol oxidation reaction. X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), atomic force microscopy (AFM), transmission electron microscopy (TEM), cyclic voltammetry (CV) and chronoamperometry (CA) were used to characterize the prepared catalysts. XRD and TEM results indicated that all prepared catalysts have a face centered cubic structure and are homogeneously dispersed on the carbon support with a narrow size distribution. XPS studies of the catalysts indicated the existence of two types of platinum (Pt (0) and Pt (IV)). Electrochemical measurements demonstrated that the highest electrocatalytic activity was observed for Pt nanocatalysts stabilized by dimethylhexylamine. The main reasons for this result could be due to an increase in electrochemical surface area, Pt(0)/Pt(IV) ratio, percent platinum utility of this catalyst.

Keywords: *methanol oxidation; platinum nanoparticles; fuel cells;*

P-0640

MICROWAVES, MATERIALS, SOLVENTS AND CATALYSIS GREEN CHEMISTRY AT THE UNIVERSITY OF YORK

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www.york.ac.uk/greenchemistry

The Green Chemistry Centre of Excellence (GCC) at the University of York for many years has worked hard to establish a leading position internationally in green and sustainable chemistry. Some 70 people are based in the GCC including, MSc and PhD students, postdoctoral fellows, core academics, senior researchers, technical staff, core management, administrative staff and network personnel. In order to manage the large and diversely funded number of projects and people, four technology platforms (TPs), an education platform and a networks platform facilitate the delivery of our research, education, networking and industrial liaison activities. The TPs include “Renewable Materials” in particular the physical and chemical modification of naturally abundant materials, especially polysaccharides. “Clean Synthesis and Platform Molecules” covering the use of heterogeneous catalysts, elemental sustainability and alternative platform molecules. The “Natural Solvents” has specific interest in non-petrochemical, supercritical and liquid carbon dioxide as an extraction, fractionation and reaction medium. Projects include wax extraction from agricultural and food waste for personal care applications, the synthesis of flavour and aroma molecules using in-situ biocatalysis and modelling of “drop-in” bio-derived replacement solvents. The microwave chemistry platform incorporating the new “Biorefinery Microwave Demonstrator” brings together our interest in microwave-assisted chemistry with the conversion of biomass (e.g. forestry and agricultural wastes, food waste, etc) to useful products in addition to a long standing interest in microwave assisted synthesis. The Biorenewables Development Centre, a joint venture between Green Chemistry and the Centre for Novel Agricultural products, launched in Spring 2012, allows the work of the green chemistry centre to be scaled up to multi-kilo scale. The centre contains a range of scale up equipment including scCO2, fermentations, AFEX, microwave pyrolysis and distillation at demonstrator scale.

Keywords: *Microwave; Renewable; Green Chemistry; Clean synthesis; alternative solvents;*

P-0641

RING-OPENING METATHESIS POLYMER BASED ON DICYLCOPENTADIENE AND TETRACYCLODODECENE

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Cyclopentadiene (CPD) or its dimer, dicyclopentadiene (DCPD), is one of the major component in the C5 stream of naphtha creaking. However, until now, most C5 streams have been incinerated as fuels instead have been used as chemical sources. An approach for the increase the value of CPD/DCPD is the synthesis of tetracyclododecene from CPD with olefin and uses it for the production of high value polymer products. In this study, we synthesized cycloolefin polymers (COPs) composed of tetracyclododecene (TCD) and DCPD using W-based ROMP catalyst and Ni-based hydrogenation catalyst and characterized their structures and some chemical properties using FTIR, 13C-NMR, GPC, DSC and UV.

Keywords: *Polymerization; Metathesis; Hydrogenation; NMR spectroscopy; CPD/DCPD;*

P-0642

AN EFFICIENT VISIBLE-LIGHT-SENSITIVE CU-GRAFTED TIO_2 PHOTOCATALYST

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Titanium dioxide (TiO_2) is one of the most used photocatalysts for the degradation of environmental pollutants. However, the main drawback of TiO_2 is lacking of visible light utilization which limits its practical application. Recently, metal ions (Cu, Fe, Cr and Ce) grafted TiO_2 has found to be an efficient way to solve the problem because they are visible light sensitive. In this study, the microwave-assisted impregnation method for preparation of Cu-grafted TiO_2 photocatalysts was reported. Parameters including reaction time and temperature were discussed in synthesized photocatalyst. In addition, UV-Vis diffuse reflectance absorption spectra and ICP-OES were used for the characterization of band-gap and for determination of weight percentage of as-synthesized Cu/TiO_2, respectively. The optimal condition for preparation of microwave-assisted Cu/TiO_2 is the dispersion of 250 mg P25 into 5 mL $CuCl_2$ solution and heated at 120 degree C for 0.2 min. From UV-Vis diffuse reflectance spectra results, the absorption intensity of TiO_2 starts to increase at 385 nm which is corresponding to the interband transition of P25 (3.2eV). In addition, another absorption region of Cu/TiO_2 around 700-800 nm which indicates the Cu d-d transition, is observed. It can be ascribed to the direct interfacial charge transfer from the valence band of TiO_2 to Cu. The ICP-OES result shows that the weight ratio of Cu/TiO_2 is in the range 0.005~0.008%. Moreover, the photoactivity of the visible light activated Cu/TiO_2 photocatalyst was studied by the photo-decomposition of sulfamethoxazole (SMX). The synthesized Cu/TiO_2 have the better photocatalytic activity toward SMX than that of Degussa P25, and the pseudo-first-order constant for SMX photodegradation by Cu/TiO_2 is 14 times higher than that of P25 under illumination of 465 nm visible light, clearly showing the excellent visible-light-driven ability of the Cu-grafted TiO_2.

Keywords: *Cu; TiO_2; visible light; sulfamethoxazole;*

P-0643

SYNTHESIS OF GLYCIDOL FROM GLYCEROL CARBONATE USING IONIC LIQUIDS

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Glycidol, 2,3-epoxy-1-propanol, is used to a considerable extent in the textile, plastics, pharmaceutical, cosmetics, and photochemical industries. Conventionally, glycidol has been produced industrially by oxidizing allyl alcohol in the presence of an oxidizing agent and a catalyst. Recently, focus has also been paid to the synthesis of glycidol from glycerol carbonate which is one of the value added material based on glycerol. In this study, we conducted thermal decarboxylation of glycerol carbonate for the synthesis of glycidol. We found that some kinds of ionic liquids showed high catalytic activities for this reaction and elucidated the catalytic activities of ILs were closely related to the hydrogen bond basicity of the anions of ILs.

P-0644

INFLUENCE OF SILICA-SUPPORTED IMIDAZOLIUM SALT ON CONDUCTING BEHAVIORS OF POLYMER COMPOSITE ELECTROLYTES BASED ON POLY(ETHYLENE OXIDE)

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Polymer composite electrolytes (PCEs) are an alternative to liquid combustible systems because they possess superior voltage, temperature and mechanical stability. In this study, PEO/PMMA polymer matrix containing modified fillers were studied in order to enhance an ionic conductivity and interfacial properties. The fillers were modified by attaching an ionic liquid (IL) functional group. The fillers were the immobilized 1-propyl-3-n-butyl--imidazolium bromide with amorphous silica (PBIm-AS). The addition of PBIm-AS fillers in polymer electrolytes has resulted in high ionic conductivity at room temperature. The crystallinity structure and morphology of the polymer composite electrolytes were measured using differential scanning calorimetry (DSC)/X-ray diffraction (XRD) and scanning electron microscope (SEM). Ionic conductivity was measured by an AC impedance method. The enhanced ionic conductivity was dependent on the decreased crystallinity and the changed morphologies.

Keywords: *Conducting materials; Electrochemistry; Energy conversion; Electron transport; Polymers;*

P-0645

EXFOLIATION AND REDUCTION OF GRAPHITE OXIDE BY ELECTROSTATIC METHOD AND THEIR ELECTROCHEMICAL BEHAVIORS

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Carbon materials including graphene can meet the request of EDLC electrodes. Graphene nanosheets (GNS) are predicted as an excellent support material due to high surface area and remarkable conductivity. Graphite oxide is electrically insulating and various reduction methods have been developed to restore its electrical conductivity. Chemical reduction using agents such as hydrazine, NaBH4 and ethylene glycol have been used to reduce GO (Graphite oxide) or graphene oxide exfoliated from GO. Also, researchers reported microwave exfoliated GO (MEGO) and thermally exfoliated GO (TEGO) to get highly reduced GO having high surface area structures. A flash-assisted reduction of films composed of graphene oxide platelets and their polymer composites has been reported. Herein, we report preparation of exfoliated and reduced GO by treating an electrostatic method. GO precursor changed black fluffy reduced GO powder by simple electrostatic force. As-prepared powder showed specific surface area of 516m^2/g, higher than the value (464m^2/g) of MEGO powder. Using the exfoliated graphite oxide, we studied electrochemical behaviors for an application of supercapacitors.

Keywords: *Conducting materials; Electrochemistry; Energy conversion; Electron transport; Graphene;*

P-0646

SYNTHESIS OF SUCCINIC ACID DERIVATIVES UNDER MICROWAVE IRRADIATION

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Dioctyl succinates and succinic anhydride were synthesized from succinic acid in the presence of a cation exchange resin, Amberlite IR-120. The synthesis of dioctyl succinate from succinic acid and octanol was perfomed in 18 h reflux condition with Amberlite IR-120 and the isolated yield of product was over 90 %. For the synthesis of succinic anhydride, succinic acid was refluxed in isopropenyl acetate for 18 h with Amberlite IR-120 as a catalyst. The long reaction time was significantly reduced to less than 10 min under microwave irradiation. We will discuss the chemical transformation using microwave irradiation method and the reusability of catalyst.

Keywords: *Catalyst Reuseability; Microwave Irradiation;*

P-0647

WATER-SOLUBLE TIN(IV) PORPHYRINS AS PHOTOSENSITISERS FOR ARTIFICIAL PHOTOSYNTHESIS

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Light-driven water-splitting into hydrogen and oxygen is a concept for sustainable energy generation. This concept is inspired by basic principles of photosynthesis, the process where solar energy is converted into chemically stored energy in nature. *In vivo*, chlorophyll molecules act as light absorbing molecules and electron transfer agents. They generate both the high oxidising potentials for water-oxidation and the strong reducing agents for $NADP^+$-reduction.

We study the water-soluble tin(IV) porphyrins dichlorido-5,10,15,20-tetrakis(*p*-carboxyphenyl)-porphyrinato-tin(IV) (SnTPPC) and dichlorido-5,10,15,20-tetrakis(*p*-sulfophenyl)-porphyrinato-tin(IV) (SnTPPS) as possible mimics for chlorophyll dyes. The compounds show favourable redox potentials to act as photosensitisers in an artificial system for light-driven water-splitting. We tested the ability of these synthetic porphyrins to act as photosensitisers in photocatalytic model systems and especially detected promising rates for light-induced H_2 formation in a photocatalytic system developed by Krüger and Fuhrhop.[1] Details on possible mechanisms, the reaction kinetics, photosensitiser stability and the use of different electron donors will be presented.

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Keywords: *Bioinorganic chemistry; energy conversion; homogeneous catalysis; porphyrinoids; water splitting;*

P-0648

MOLYBDENUM-INFLUENCED POROSITY IN RF XEROGELS

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Carbon aerogels that are simultaneously macro- and mesoporous offer advantages over other forms of adsorbents for applications that demand rapid access to the internal surface. Such carbons can be synthesized from resorcinol and formaldehyde under controlled conditions, like concentration, stoichiometric ratio, catalyst, pH, etc. The porosity of dried esorcinol-formaldehyde (RF) gels is conserved during the conversion to carbon. Due to their sol-gel preparation method these RF gels they can be easily doped with metals, which can enhance their catalytic and adsorption properties. Moreover, they provide an additional means of tuning the porosity of the system. In this work we focus on the effect of molybdenum, which is widely used as catalyst, e.g., in hydrocarbon industry.

Molybdenum was added as aqueous ammonium-heptamolybdate solution to the RF hydrogel prepared in a glass cylinder after a 1-week ageing process. After 24 hours diffusion the hydrogel rods were cut into 10 mm long pieces and air-dried to obtain Mo-doped xerogels. Low temperature nitrogen adsorption and scanning electron microscopy supported energy-dispersive X-ray spectroscopy (SEM/EDX) were used to characterize the morphology and the molybdenum content of the samples.

Increasing the amount of Mo reduces the porosity (all class of pores) but the typical size of the mesopores is conserved.

P-0649

THE IMPACT OF THE RECONSTRUCTION EFFECT ON THE STRUCTURAL PROPERTIES OF MGXALLDH MATERIALS AND THEIR CATALYTIC ACTIVITY IN THE OXIDATION OF CYCLOHEXENE

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Many papers concerning the preparation, characterization and utilization of layered double hydroxides in different applications have been published[1, 2]. One of the goals has been to provide new insights on the role played by the LDH-like phase and the impact of the reconstruction through "memory effect" presented by LDH-like materials on the selectivity to cyclohexane epoxide during the oxidation of cyclohexene. The catalytic activities of parent Mg_xAl-LDH materials ($x=1,3,5,10$), have been compared with those of the corresponding mixed oxides and the corresponding reconstructed LDH-structures. The parent LDH were obtained by co-precipitation of Mg and Al nitrates with a base solution at pH = 10 under low supersaturation conditions; Mg_xAl-MO by thermal decomposition at 460 °C under air atmosphere; Mg_xAl-RLDH by hydration with bi-distillate water at room temperature. All catalysts were characterized by XRD, DRIFTS, BET and determination of base sites. The oxidation of cyclohexene was performed using two different oxidation agents: **i**) H_2O_2 in a reaction mixture containing cyclohexene, acetonitrile and acetone and **ii**) molecular O_2 in a reaction mixture containing cyclohexene, isobutyraldehyde, and acetonitrile. It has been found that LDH-like materials were poor catalysts for the oxidation of cyclohexene with H_2O_2 while they exhibited higher catalytic activity in the oxidation of cyclohexene with molecular O_2. This behaviour may be a consequence of the different reaction mechanisms involved, depending on the oxidation agent and the reaction mixture employed. The solids having Mg/Al = 3 were better reconstructed and higher catalytic activities. The variation order of the catalytic activity could be related to the variation of the basicity and surface areas of the solids.

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Keywords: *layered double hydroxides; hydrotalcites; base materials; oxidation;*

P-0650

SELECTIVE RECYCLING OF MOLYBDENUM FROM SPENT HYDRODESULFURIZATION CATALYSTS USING ENVIRONMENTAL-FRIENDLY APPROACHES

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Recovery of valuable metals from spent hydrodesulfurization (HDS) catalysts avoids their disposal in the environment and permits the production of metal values from secondary resources.

The goal of this work was to study the selective leaching of Mo from HDS spent catalysts, under mild alkaline conditions using microwave- or ultrasound- assisted conditions, and to recover it through an environmental and economically attractive process.

Spent catalyst, containing Ni, Mo and Al, was roasted and its metal content was determined. Mo leaching was performed using aqueous NaOH at constant solid-liquid ratio under the following conditions: (**i**) microwave-assisted leaching by varying [NaOH] and number of cycles (30 seconds/cycle) and (**ii**) ultrasound-assisted leaching; for comparative purposes, (**iii**) conventional approach using a thermostatic bath, where temperature, time and [NaOH] were varied.

Experiments in the bath at 80ºC, 120 minutes, showed that Mo dissolution increases with [NaOH], however Al extraction is also enhanced: 92% Mo, 19% Al, using 20g/l NaOH. Lower [NaOH] (10g/l) leads to a more selective leaching of Mo, though the yield is affected: 77% Mo, 7% Al. Applying microwave energy (4 cycles), at the same [NaOH], Mo leaching is improved with no enhancement in Al removal (89% Mo, 6% Al) which increases Mo selective leaching. Mo and Al leaching results, obtained under ultrasound-assisted conditions, were similar to the conventional ones, obtained at room temperature, but with shorter processing times.

Al present in solution was precipitated at pH 8 and separated. Mo was recovered as $SrMoO_4$, a promising product in the field of optical devices and lasers, with high yield (96%) and purity (>99%).

These results show that microwave-assisted leaching, using mild alkaline conditions, may be an interesting alternative in the Mo leaching from spent catalysts; moreover, $SrMoO_4$ can be produced at high purity from secondary resources using a low-cost process.

Keywords: *Molybdenum; Microwave chemistry; Ultrasound; Strontium; Spent catalysts;*

P-0651

ALGINATE-SUPPORTED PALLADIUM NANOPARTICLES: A GREEN AND RECYCLABLE HETEROGENEOUS CATALYST WITH REMARKABLE ACTIVITY FOR THE SUZUKI-MIYAURA REACTION

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Alginates are polysaccharides produced by brown algae mainly, constituted of (1-> 4) linked b-d-mannuronic (M) and a-l-guluronic (G) residues, they form ionotropic gel by complexation of divalent cations. Drying the gel under CO_2 supercritical conditions afford highly dispersed materials.[1] This aerogel formulation is particularly adapted for supporting metal particles. Indeed, the gelling cations in a M-alginate gel can be exchanged by palladium cations. Palladium is easily reduced by ethanol; therefore, in situ formation of palladium particles supported on M-alginate occurs during the process leading to the aerogel. The process affords a double homogeneity in bead size and metal distribution inside the bead. This strategy applied to many gelling metals M^{n+} allows the straightforward preparation of a panel M^{n+}/PdNP/alginate gels[2]. The resulting bimetallic hybrid catalysts combine the textural properties of alginate, the high catalytic activity of palladium nanoparticles and the presence of a second metal species that might serve to co-catalysis. Indeed, only 10 ppm of Pd (< 0.01% w/w) in EtOH at 70°C were required to undergo complete conversion of reactants to biaryl product in only 3 hours. In same conditions but with 1 ppm PdNP, TurnOver Number is close to one Million (910 000) and the TurnOver Frequency is close to 10 reactions by second (TOF 35 000 h^{-1}).

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Keywords: *Natural products; Cooperative effects;*

P-0652

CARBON MONOXIDE OXIDATION OVER SNO_2 20WT%-CEO_2 MIXED OXIDE

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Ceria with appropriate dopants (e.g. SnO_2, CuO) has been widely used as catalyst for heterogeneous oxidation processes such as CO oxidation to CO_2. The aim of this work was to prepare the SnO_2-CeO_2 catalysts in order to increase the oxygen storage/release capacity of single oxides. Moreover it was aimed to investigate the redox properties of the mixed oxide and its catalytic activity with respect to their potential application for environmental oxidation processes. The adsorption properties of the surface layer with CO probe molecule was studied by electrical conductivity measurements in operando condition. CO oxidation was carried out in a mixture of CO and O_2 (1:1) diluted with helium. The experiments were carried out in the temperature range of 25°C up to 400°C.

The obtained data showed that in the presence of oxygen the conversion of CO to CO_2 was 99% over tin oxide-containing sample at 400 °C in comparison with pure ceria and tin dioxide samples in which case the CO conversion was about 88 and 84 % respectively. It is to be noted that CO is also converted even in the absence of oxygen, however, obviously the obtained amount of CO_2 was smaller; (less than 40%) over SnO_2 20wt%-CeO_2, about 3% over CeO_2 and about 4% over SnO_2. It indicates that the lattice oxygen is involved in the CO conversion which was also supported by electrical conductivity measurements.

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Keywords: *Heterogeneous catalysis; Oxidation; Redox chemistry;*

P-0653

PRODUCTION OF LIGHTWEIGHT AGGREGATE BASED ON NATURAL POZZOLANIC AND WASTE MATERIALS

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The physical and chemical properties of the lightweight aggregates (LWA) obtained by the thermal treatment of raw composition based on natural pozzolanic material, waste glass, suitable polymer and wooden dust are presented. The production process of LWA was consisted of raw material preparation, plastic shaping - extrusion, granulation and thermal treatment at the final firing temperature. The final temperature (T = 1020°C) was chosen based on the appropriate mechanical and physical properties of the designed LWA pellets. Properties of raw natural pozzolanic material were examined by using, DSC/TG, dilatometry, while waste glass was characterized by chemical analysis and XRF.

The particle size distribution of the LWAs was unimodal ($d \approx 5$ mm). Textural and mechanical properties of LWA pellets were examined by water absorption, mercury porosimetry and compressive strength. The microstructure of LWA pellets was characterized by SEM analysis while phase composition during thermal treatment was studied by using high temperature XRD analysis. Thermal conductivity of unbound, fired LWA pellets was determined by measuring the amount of axially transferred heat in the stationary state.

The obtained value of the LWA thermal conductivity is suitable for the production of structural concrete blocks with improved thermal insulating properties. Due to their high porosity and appropriate compressive strength values, the designed LWA could be used in the production of concrete blocks.

Keywords: *Materials science; Ceramics; Electron microscopy; X-ray diffraction; Thermal conductivty;*

P-0654

FROM LAYERED BASIC ZINC SALTS TO ZNO HOLLOW SPHERES BY AN ECO-FRIENDLY SONOCHEMICAL PROCEDURE

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The attractive and unique characteristics of ZnO, a bio-safe and bio-compatible semiconductor, besides its huge variety of morphologies, made it a key functional material for applications in different fields. Among its structures, ZnO hollow spheres have shown a great potential for use in the delivery of drugs, catalysis, chemical storage, photoelectric materials and so on.

Layered basic zinc hydroxide compound (LBZS) that contain both carbonate and acetate as intercalated anions have been obtained and deposited on starch-derived carbonaceous template by a new eco-friendly sonochemical procedure with a low power sonicator, using nonbasic zinc acetate aqueous solution. The synthetic route involves the hydrolysis and polymerization of the *in situ* formed complexes. Calcination treatments (600°C, 1h) of the LBZS and core/shell materials afforded ZnO porous sheets and hollow spheres respectively. The morphology, composition and phase structure of the precursors and their decomposition products were characterized by infrared spectroscopy, thermal analysis, scanning electron microscopy (SEM) and X-ray diffraction (XRD). The LBZS consists of lamellar structure with two interlayer distances (13.70 and 19.34 ?), poorly ordered, both the XRD pattern and SEM images being characteristic for turbostratic materials. The acetate anions are intercalated as free anion and monodentate ligand, while the carbonate ones behave as bidentate ligand. The obtained ZnO preserves the sheet-like morphology of the layered precursors, presenting uniform pores and pore density while the core/shell materials attained after deposition represent efficient precursors for hollow ZnO spheres, allowing high heating rates treatments without altering the hollow sphere morphology. The obtained hollow spheres are composed by sintered ZnO nanocrystallites with mean crystallite sizes values strongly depending on the used heating rate.

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Keywords: *environmental chemistry; layered compounds; green chemistry;*

P-0655

SUBCRITICALLY DRIED CELLULOSE – BASED CARBON AEROGELS WITH HIGH SURFACE AREA

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Carbon aerogels are fascinating materials with large open pores, high values of specific surface area and low densities. Generally these materials are prepared from appropriate precursors by their condensation to small polymer particles followed by gelation. Spongelike network is obtained and the pores are filled usually with water or with alcohol [1]. Drying of wet gels is critical operation, because capillary effect causes collapse of nanostructure porous network. That is the reason for usage supercritical drying or freeze – drying methods [2].

Aim of our work was to replace established but difficult drying methods in the cellulose based carbon aerogels preparation with simple drying under atmospheric conditions. Aerogels from cellulose or cellulose acetate were prepared by dissolving these polymers in suitable solvents such as aqueous calcium thiocyanate [3] or mixture of sodium hydroxide with urea and water [4]. Prepared materials were either dried by freeze-drying or left to dry at laboratory conditions. This simple attempt lead to expected results – surface area of freeze dried samples was significantly higher (up to 460 $m^2 g^{-1}$) then surface area of samples dried on air (below 20 $m^2 g^{-1}$). We tried to use another ionic liquid N-methyl-morpholine-N-oxide [3] but obtained materials showed similar results after drying (25 - 270 $m^2 g^{-1}$). In another case of preparation of these materials, cross – linking agent PMDI (polymethylene polyphenylpolyisocyanate) [5] was used and obtained materials were freeze – dried and dried under ambient conditions. In both cases, values of surface area were higher than 600 $m^2 g^{-1}$. In this work, it was found that we can make these cellulose – based materials without supercritical or freeze – drying due to use of cross – linking agent PMDI. Usage of this compound sufficiently strengthens structure of these materials, which do not collapse during drying under ambient condition.

Keywords: *Cellulose - based carbon aerogels; cross - linking; subcritical drying;*

P-0656

ENZYME-CATALYSED RESOLUTION OF N-BOC-3-HYDROXY-4-PHENYLPYRROLIDINE IN SUPERCRITICAL CARBON-DIOXIDE

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The preparation of enantiopure drug intermediates is a topic of great importance in research. While there are numerous chemical methods for producing pure enantiomers, using enzymes has many advantages compared to other processes. The enzymes most commonly used for kinetic resolution are lipases, some of which could be active in supercritical media as well. Supercritical carbon-dioxide (scCO_2) is a solvent with industrial applications. Among its many advantages is the fact that its properties (density, viscosity) can be modified in a wide range by changing the pressure and temperature. Due to its relatively mild critical parameters, the decomposition of the product and substrate can be avoided. After depressurization, carbon-dioxide becomes gaseous, thus potentially yielding a solvent-free product.

The kinetic resolution of N-Boc-3- hydroxy-4-phenylpyrrolidine was investigated by CALB-catalysed (lipase B from *Candida Antarctica*) acylation with vinyl acetate in scCO_2 in a batch reactor. The substrate:CALB mass ratio was 2:1. Vinyl acetate was used in excess. The samples were analyzed by chiral gas chromatography. The reaction progress was examined at different pressures (10–20 MPa) and temperatures (35–65°C) according to a 3^2 experimental design.

In this reaction at 15 MPa and 50 °C, enantiopure (3*R*,4*S*)-N-Boc-3-hydroxy-4-phenylpyrrolidine ($ee \geq 99.9$ %) was achieved with good yield (Y~60 %) and moderate enantioselectivity (E~50). Increasing the temperature increases both the enzyme activity and the enantioselectivity, while enantioselectivity has an optimal pressure range around 15 MPa. Increasing the pressure has a negative effect on the reaction rate in the examined range.

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Keywords: *kinetic resolution; supercritical fluids; enzyme catalysis;*

P-0657

METAHESIS REACTIONS PERFORMED IN PURE WATER, USING COMMERCIAL CATALYSTS

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Olefin metathesis is an interesting, atom-efficient, and very valuable synthetic transformation, mainly performed in organic solvent. Subsequently, fewer studies on metathesis reactions in pure water as solvent were done.

We showed that olefin metathesis can be performed very efficiently in pure water without exclusion of air, using standard Grubbs-type catalyst. Beside activity, also stability tests were determined by standard RCM reactions.

Addition of host molecules such as calix[*n*]arenes can boost the reactivity by a supramolecular interaction with in water protonated Cy3P which is released in the activation step of the catalysts.

Keywords: *Metathesis; water chemistry; supramolecular chemistry; ion pair;*

P-0658

ONE-POT SYNTHESIS OF PARACETAMOL VIA THE CATALYTIC REDUCTIVE CARBONYLATION OF P-NITROBENZENE IN ACETIC ACID-WATER AS A SOLVENT

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Paracetamol (N-(4-hydroxyphenyl)acetamide) is a major ingredient in numerous cold and flu medications due to its analgesic and antipyretic properties. A number of commercial methods of paracetamol manufacture are currently in use around the world. Some commonly used processes start from chlorobenzene, phenol or nitrobenzene. All the industrial processes actually used, however, show several drawbacks. For instance, they are based on multistep routes which sometimes lead to poor overall yield, or show serious effluent problems. The increasingly stringent environmental legislation has generated a pressing need for cleaner methods of chemical production, for instance introducing technologies that reduce or, preferably, eliminate the generation of waste and avoid the use of toxic and/or hazardous reagents and solvents. According with this, we propose a new approach for the synthesis of paracetamol: by using Pd(II)-diphosphine catalyst precursors, in acetic acid-water as a solvent, we obtain paracetamol with high selectivity from nitrobenzene in one-pot. At 140 °C and under 45 atm of CO, p-nitrobenzene is completely converted to paracetamol and N-phenylacetamide. The latter is the major by-product of the reaction (ca. 15 molar %, under such reaction conditions) and also an interesting target for the pharmaceutical industry. The selectivity is influenced by several variables such as solvent composition (H_2O-acetic acid ratio), temperature and batch time. The high temperature and the increase of reaction time favor the acetylation reaction, which occurs in-situ when p-aminophenol and aniline readily form from p-nitrobenzene/CO/H_2O. Such reaction is proposed as a new sustainable alternative to the synthesis of paracetamol. The absence of chlorobenzene (chlorine-free chemistry), the use of efficient catalysts and the possibility to realize a single step process, make this reaction interesting to be evaluated as a possible alternative to the multi-steps industrial processes actually used.

Keywords: *Carbonylation; Reduction; Homogeneous catalysis; Sustainable Chemistry;*

P-0659

CATALYTIC DEPOLYMERIZATION OF LIGNIN UNDER ULTRASOUNDS CONDITIONS

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Lignin is an aromatic polymer including three main phenylpropane units, namely *p*-coumaril, coniferyl and sinapyl alcohol which are linked by C-C or C-O-C. Recently Lavoie et all have reported depolymerisation of lignin in the presence of NaOH[1]. However, using homogenous catalysts is necessary a purification step of the reactions products that is a non-friendly environmental process producing high amounts of waste waters. A solution to this problem can be the use of heterogeneous catalysts because they can be recovered at the end of the reaction by centrifugation providing green, recyclable catalytic systems.

In this study we investigated the influence of the crystallographic phase of Ru (RuNi, RuNiO and Ru/Al_2O_3) in conversion of lignin to low molecular weight compounds under ultrasounds conditions. RuNi and RuNiO were prepared by replacement reaction between nickel or nickel oxide and $RuCl_3$ in aqueous solution[2] while Ru/Al_2O_3 was prepared by wet impregnation of mesoporous alumina with a $RuCl_3$ aqueous solution. These materials were characterized by several techniques like: XRD,BET,XPS,etc. Lignin tested in this study was extracted from mischantus plants under both acid and basic conditions[3] and was characterised by DRIFT and TGA/DTA. Depolymerisation of lignin was carried out under bubling hydrogen in special designed ultrasound reactor. The reaction products analyzed by LC-MS had molecular weights with m/z below 1000 g/mol, that confirmed the depolymerization of lignin.Among the investigated catalysts RuNi led to an advanced depolymerisation of lignin.

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Keywords: *lignin; ultrasounds; heterogeneous catalysts;*

P-0660

IMMOBILIZATION MECHANISMS OF PB(II) ADSORPTION ONTO COALS, CARBONS AND CARBON AEROGELS

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Removal of heavy metal ions from aqueous solutions is essential in terms of environmental and human health protection. One of the most used techniques is adsorption onto different carbon materials.

The aim of this contribution is to point out different immobilization mechanisms of Pb(II) adsorption onto various types of carbon materials (coals, carbons and carbon aerogels).

Two types of natural coals were used - oxidative altered bituminous coal (A) from the Upper Silesian Coal Basin and subbituminous coal (H) from the North Bohemian Coal Basin. Also commercial activated carbon (AC) from Hru‰ovské závody (Czech Republic) was tested. Carbon aerogels (CA) were prepared by sol-gel polycondensation, subcritical drying and pyrolysis of resorcinol and formaldehyde with or without addition of nitrogen containing precursor. Batch adsorption experiments and also pH solution measurements before and after adsorption were conducted in order to study immobilization mechanisms of Pb(II) on these materials.

It was noticed that decisive (majority) role in adsorption of Pb(II) on the sample A has mineral composition when the crucial elements were found to be magnesium and calcium. As minority mechanisms for sample A are expected to be complexation and ion-exchange. Adsorption onto H can be described by different adsorption mechanisms - ion-exchange and complexation. Also mineral composition can be taken into account in the case of sample H. Immobilization of Pb(II) onto HS occurs on the graphene structures without releasing of hydrogenous ions. Basic mechanism connected with CA is expected to be ion exchange, but there is probably some additional mechanism (e.g. complexation) for N-doped CA which increase the adsorption capacity for Pb(II) in comparison with non-doped samples.

It can be concluded that immobilization mechanism of Pb(II) is dependent on the carbonaceous material used for adsorption.

Keywords: *immobilization mechanism; Pb(II) adsorption; carbon material;*

P-0661

CONTROLLED BIOPOLYMER ASSISTED SYNTHETIC ROUTE OF ZINC OXIDE WITH DIFFERENT MORPHOLOGIES

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Recently, the synthetic procedures that control the size, shape and dimensionality of inorganic nanocrystals materials has rapidly expanded into a promising topic of materials chemistry, due to materials unique size- and shape-dependent properties. A special place is occupied by ZnO a bio-safe and biocompatible n-type semiconductor which tendency to grow into a variety of aesthetic morphologies has induced great interest to explore simple methodologies of developing such nanoarchitectures. On the other hand, over the past years, the great concern on environment protection determined the development of green strategies for nanomaterials' *designing* and synthesis. Polysaccharides thanks to their unique combination of environmentally friendly features and functional versatility represent an appropriate choice, with great potential as additives in materials synthesis.

Herein we report an original, green and low temperature (<80ºC) precipitation route of zinc oxide, carried out in the presence of a soluble cellulose derivate. Altering the experimental conditions (reaction pH, temperature, time, precipitation agent and polysaccharide/metallic cation ratio) spindle- and pencil-like morphologies of ZnO characterized by different sizes, surface areas and interesting photoluminescence properties were obtained. The photocatalytic capacity evaluated towards some organic contaminants degradation was also tested.

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Keywords: *Green chemistry; Polymers; Semiconductors; Synthesis design; Luminescence;*

P-0662

SYNTHESIS OF NEW MONO AND DINUCLEAR IMIDAZOLIUM SALTS

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Imidazolium salts are an important class of organic compounds with a plethora of modern applications in e.g. as solvent, catalysts or as precursors for *N*-heterocyclic carbens (NHC's).[1-3] Such uses of these heterocycles are facilitated by the fact that they are easily synthesized and their properties can be fine-tuned by changing the substituents on the heterocyclic skeleton or changing the counter anion.

First we want to present the synthesis of some imidazolium salts varying the number of imidazolium moieties included, and substituent at the ring nitrogen. A special focus lies on the influence of the anion and cation on the physical and chemical properties.

Second we present the synthesis of different imidazoliumcarboxylates. The imidazolium salts where deprotonated with a strong base and afterwards carbon dioxide was bubbled through the solution. The formed imidazolium carboxylates were characterized by NMR, mass, IR and, to determine the thermal stability, by TGA/DSC.

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Keywords: *Ionic liquids; carbon dioxide fixation;*

P-0663

IMPROVING THE WATERPROOFING MATERIAL'S PERFORMANCE PROPERTIES BY USING NATURAL FILLERS AND INDUSTRIAL RESIDUES

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Background: Water in the form of vapor,liquids and solids presents below-grade construction with many unique problems.Water causes damage by water transmission through porous surface, by direct leakage in a liquid state and by spalling of concrete floors in a frozen or solid form. In construction, a structure needs waterproofing since concrete itself will not be watertight on its own.

Objectives: Solutions to the economic and environmental impacts of the construction industry have largely focused on choosing replacement materials at the level of products. The sole aim of this study focuses on the possible system improvements of the already advantageous cement based waterproofing material.

Method: This study looks at the effectiveness of six powdered natural fillers and industrial waste materials after 28 days of curing at: 5.0%, 25%, 50%, 75% and 100% w/w on the whole composition.

In this study, utilization of natural pozzolanic fillers and industrial waste materials in the production of cement based waterproofing materials was investigated. For this purpose, Karakaya bentonite (B) ; Seyitgazi volcanic tuff (V) and Karaman diatomite (D) were used as natural puzzolanic fillers ; waste tire rubber from tire factory (R), tile powder from tile factory (T), waste marble powder from marble factory(M) were used as a industrial waste materials. Three types of pozzolans (B+V+D) and three type of waste materials (R+T+M) were added to cement pastes in.

Results and Conclussion/Application to practice: It was observed that, a comparison with the common fillers, waste tire rubber and marble powder using as a filler enhance tensile and compressive strengths at the age of 7 and 28 days, capillary absorption and permeability to water ability. Economically,new product with produce with marblr powder and waste tire rubber at the same ratio provide approximately % 27 per kg.(Prices may show variation due to the market conditions.)

Keywords: *industrial residues; waterproofing; natural fillers; green materials;*

P-0664

DEVELOPMENT AND APPLICATION OF NOVEL BIOINSPIRED IONIC LIQUIDS

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Biological molecules are considered as building blocks of life. The understanding and use of their chemistry represents a crucial role in modern research science[1]. In last decades, Ionic Liquids (ILs) have emerged as a possible environmentally benign alternative to common organic solvents, due to use in a variety of areas[2]. In this context, Novel Functional Bioinspired ILs (FBILs) based on the incorporation of relevant biological molecules by simple dissolution (e.g. ILs and cyclodextrins) or by sustainable synthetic combinations (e.g. chiral ILs based on aminoacids such as L-cysteine derivatives) have been developed.

The main goal is related with the development of novel Chiral biomaterials based on the interaction of biocompatible ILs and cyclodextrins as well as the preparation of L-cysteine derivatives as chiral ILs. Applications of this novel Chiral ILs include their use for chiral recognition processes and chiral media for asymmetric catalysis[3].

Two different approaches have been investigated: (**i**) dissolution and interaction studies of α-, β- and γ- cyclodextrins (CDs) with several ILs. Their dissolution performance and interaction behavior have been studied. Novel biomaterials based on simple combination of ILs and CDs can be applied for host-guest and drug delivery processes[4]; (**ii**) preparation and characterization of novel chiral ILs based on L-cysteine derivatives such as S-methyl-L-cysteine and S-carboxymethyl-L--cysteine combined with appropriate counter-ions. The most promising chiral ILs has been applied for enantiomeric resolution and asymmetric catalytic reactions.

Novel biocompatible materials based on the combination of ILs and CDs can be explored for relevant chiral discrimination or separation processes. Novel L-cysteine ILs have been tested for resolution of racemates as well as chiral media for asymmetric aldol and Michael reactions[5]. Their efficiency should be dependent of the combination of L-cysteine as cation or anion with appropriate counter-ions.

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Keywords: *Amino acids; Ionic liquids; Green chemistry; Asymmetric catalysis; Chirality;*

P-0665

PROPERTIES OF LIGHTWEIGHT AGGREGATE BASED ON COAL FLY ASH

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The paper presents the results of physical and chemical properties of lightweight aggregates (LWA) obtained by the thermal treatment of raw composition based on fly ash, supplied by electric plants from Serbia. The final temperature ($T = 1140^{o}C$) was chosen based on the appropriate mechanical and physical properties of the designed pellets.

The particle size distribution of the LWAs was unimodal ($d \approx 16$ mm). Their textural and mechanical properties were examined by water absorption, mercury porosimetry and compressive strength. Leaching of mineral salts of the LWAs after 24h of immersion was performed with an intensive stirring. Wide range of the elements in the LWAs aqueous extract was determined by using mass spectrometry. The thermal conductivity of unbound, fired LWA pellets, is determined by measuring the amount of axially transferred heat in the stationary state. Radioactivity of dried and fired LWA pellets was examined too.

The obtained value of the LWA thermal conductivity ($\lambda = 0.0862$ W/mK, $T = 1140^{o}C$) is suitable for the production of structural concrete blocks with improved thermal insulating properties. Radionuclide reducing after thermal treatment of LWA was noticed. Due to their high porosity and high compressive strength values, the designed LWA could be used instead of the conventional aggregates in the production of concrete blocks. Consequently, a real valorization of the waste material such as fly ash in Serbia was established.

Keywords: *Materials science; Ceramics; Waste prevention; Thermal conductivty;*

P-1013

SYNTHESIS AND THERMAL TREATMENT INFLUENCE ON ZNO NANOPARTICLES LUMINESCENCE

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The potential application of ZnO requires a good control of its optical properties. The photoluminescence spectra of ZnO powders usually present two emission peaks in the UV and visible ranges. The UV emission corresponds to the near band-edge emission and the visible emission is commonly referred to as a deep-level or trap-state emission. Some specific application requires that only one luminescence peak should be present so is of great importance that one can control the luminescence properties of ZnO nanoparticles.

The magnitude and the relative intensity of these two bands are sensible tot the synthesis method and thermal treatment applied to the ZnO nanoparticles. In this paper, we present a study of a new non-basic, non-aqueous synthesis method of ZnO nanoparticles. We found that the nature of the alcohol used in the force solvolysis of zinc acetate influences the magnitude of the UV luminescence, and only marginal the intensity of the blue-green one. A correlation could be made with the molecular mass of the alcohol, and length of the carbon chain, the fluorescence intensity increasing from methanol to 1-pentanol.

The influence of the thermal treatment on the ZnO luminescence is also discussed. Both temperature and annealing time influences the magnitude and relative intensity of luminescence peaks. By increasing both parameters, we manage to increase the overall magnitude of fluorescence in ZnO nanoparticles, but we also increase the UV/Vis intensity ratio, up to 10/1.

This study provides a simple method to control the luminescence properties of ZnO nanoparticles.

Keywords: *ZnO; luminescence; thermal treatment;*

P-0666

MOLECULAR ROTORS IN MESOPOROUS MATERIALS

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Molecular rotor systems have been one of most challenging topics in the last years. Inspiring to biological molecular machines based on rotor systems, such as ATP-synthase, chemists have tried to reproduce functional nanodevices based on molecular rotors. One of the main targets in this research field was the attainment of materials wherein molecular rotors are organized in such a way that the free space around them is maximized and the rotational barrier is as low as possible.

In this work we present a first example of highly-ordered materials wherein molecular rotors are linked to the framework through robust covalent bonds, which confer both thermal and chemical stability to the final material.

We have chosen Periodic Mesoporous Organosilica (PMO) systems with crystal-like pore walls, such as *p*-phenyl, diphenylene and *p*-divinylphenylensilica, to study the rotational properties of the organic linkers pivoted between two siloxane layers. In these materials, organic moieties are organized at molecular level in the pore walls with the adjacent organic linkers posed at a distance greater than the sum of van der Waals radii. We have explored the dynamics of the molecular rotors by ^{2}H NMR spectroscopy on the deuterated aromatic moieties. In fact, ^{2}H NMR spectroscopy is a method of choice to determine the mechanism of motion. Rotational frequencies as fast as 10^8 Hz were estimated at room temperature and energy activation barriers of about 10 kcal/mol were calculated. Interestingly, we demonstrated for the first time that the rotational motion could be controlled by the presence of guest molecules diffused-in the mesopores and the materials change from a 2D rotational glass to a 2D rotational fluid behavior by increasing the temperature. In conclusion, these materials could find applications as gas-sensor systems or carriers for controlled release of stored molecules.

Keywords: *Mesoporous materials; Molecular devices; Hybrid materials;*

P-0667

STUDIES ON ULTRASOUND-ASSISTED SYNTHESIS OF HIGHLY DISPERSED MANGANESE DOPED ZINC SULPHIDE POWDERS

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Due to their special properties, the highly dispersed II-VI semiconductors account for the most investigated materials. Zinc sulphide-based materials have attracted increasing interest with respect to their applications in various domains i.e. optoelectronics [1]. Through controlling the size and the doping of zinc sulphide (ZnS) particles with manganese[2], a different material with new properties and uses could be obtained.

Because of strongly dependence of powders properties by synthesis method, a various methods have been developed for the preparation of un-doped or doped ZnS powders, methods such chemical precipitation[1] and ultrasound[3] assisted synthesis routes.

Herein we report the ultra-sound assisted synthesis of highly dispersed Mn-doped zinc sulphide powders (ZnS:Mn) with luminescent properties. Synthesis was performed from zinc-manganese acetate and thioacetamide, in aqueous medium with controlled pH. Variable manganese concentrations and different organic additives were used in order to control the morphostructural and photoluminescence properties..

ZnS:Mn samples were characterized by photoluminescence spectroscopy (PL), transmission and scanning electron microscopy (TEM, SEM), X-ray diffraction (XRD) and inductively coupled plasma optical emission spectroscopy (ICP-OES).

A correlation between the preparation conditions and powders characteristics was established.

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Keywords: *Luminescence; Chalcogens; Doping; Manganese; Nanoparticles;*

P-0668

CONTROLLING THE DISPERSION OF MONOMETALLIC NANOPARTICLES PREPARED BY WATER-HEXANE IMPREGNATION ON THE MESOPOROUS SBA-15 SILICA

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The purpose of this study is to prepare highly dispersed monometallic nanoparticles by impregnation of the mesoporous SBA-15 with nitrate precursors of copper, nickel and cobalt, and using water - hexane mixture as solvent. Three monometallic samples with 5 wt % metal loading were prepared. The calcined samples were characterized by ICP-OES, FT-IR, XRD at high and low angles, nitrogen physisorption, and TPR. Preliminary, all the catalysts were tested in the hydrogenation of cinnamaldehyde (CNA) to cinnamyl alcohol (CNOL). High angles XRD and TPR analyses displayed very high dispersion and high reducibility (T_{red} = 230 °C), respectively of the supported copper oxide. These results were reflected by the catalytic behavior, after reduction at 350 °C under H_2 flow, that shown a quite active and selective catalyst. Therefore a $X_{CNA} = 20$ mole % and $S_{CNOL} = 40$ mole % at $X_{CNA} = 10$ mole % were obtained for this catalyst. For Co/ and Ni/SBA-15 samples XRD and TPR investigations indicated two types of metal precursors. Therefore, the majority crystalline phase consisted in the corresponding oxides; typical reflections of the NiO and Co_3O_4 were identified in the XRD patterns while the TPR profiles display a first reduction peak at 480 °C for highly dispersed NiO and in low interaction with the support, and 300 °C for Co_3O_4. Also, nickel and cobalt (phyllo)silicates phases, respectively were observed in both samples and considered as additional factor which contributes to the good dispersion of metal nanoparticles. Additional information was provided by FT-IR spectroscopy which indicated a vibration band at 960 cm^{-1} attributed to Si-O vibration in 1:1 phyllosilicate. Preliminary tests in CNA hydrogenation shown active Ni/SBA-15 and inactive Co/SBA-15 catalysts.

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Keywords: *monometallic supported nanoparticles; water-hexane impregnation; hydrogenation;*

P-0669

HIGHLY DISPERSED CUCO (BI)METALLIC CATALYSTS PREPARED BY DEPOSITION-PRECIPITATION ON MESOPOROUS SBA-15 SUPPORT FOR THE CINNAMALDEHYDE HYDROGENATION

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Highly dispersed copper-cobalt nanoparticles with 5 wt % metal loading and Cu:Co weight ratio of 4:1 were prepared by deposition-precipitation (DP), using urea as precipitating agent, into the channels of a mesoporous SBA-15 support. The monometallic Cu/ and Co/SBA-15 (5 wt. %) were also prepared by DP and used as references. The resulted materials either as-made or calcined were characterized in relation to their chemical, structural, textural and reducible properties by chemical analysis, XRD, N_2physisorption, TEM/EDX, FT-IR spectroscopy, ATG and TPR. The catalytic performance of the copper-cobalt containing materials was evaluated in the hydrogenation of cinnamaladehyde (CNA) in liquid phase. The high-angle XRD patterns of mono- and bimetallic catalysts besides FT-IR spectra and ATG curves indicate the formation of phyllosilicates with very high dispersion and thermal stability as precursors of the metallic active phases. Moreover, the TPR analysis displayed reduction temperatures very close to those corresponding to phyllosilicates. However, the synthesis of such materials by DP led to partial alteration of the support mesostructure, which was shown by nitrogen physisorption and TEM. The EDX analysis carried out in various points of the catalysts shows a homogeneous distribution of the metal precursors at micrometric scale. Generally, the catalytic activity of the monometallic catalysts is in line with the characterization results. Therefore, for Cu/SBA-15, the very high dispersion of Cu^0 precursor generate an active (conversion of CNA = 40 mole % after 360 min of reaction) and selective catalyst for cinamyl alcohol (CNOL, 40 mole % at iso-conversion of 40 mole %). Due to their hardly reducible cobalt precursors, the cobalt based catalysts were less performing in the hydrogenation of CNA. However, the Co/SBA-15 displayed improved selectivity to CNOL (50 mole % at iso-conversion of 18 mole %).

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Keywords: *metal supported catalysts; copper; cobalt; cinnamadehyde hydrogenation;*

P-0670

MILD DRYING IMPREGNATION METHOD USED FOR THE PREPARATION OF MESOSTRUCTURED CATALYTIC MATERIALS CONTAINING CU, NI AND CO AS ACTIVE PHASES IN THE HYDROGENATION OF CINNAMALDEHYDE

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This study deals with the preparation of monometallic catalysts by an upgraded version of the conventional wetness impregnation method, named mild drying impregnation (MDI). Therefore, Cu, Co and Ni monometallic catalysts with 5 wt % metal loading on support were prepared by MDI on SBA-15, followed by calcination, reduction and then by characterization and testing in the hydrogenation of cinnamaldehyde (CNA) to obtain cinnamylalcohol (CNOL). For a good dispersion of the metal precursors, all impregnated samples were subjected to drying for two weeks at controlled temperature. All samples were preliminary characterized by XRD at high and low angles, nitrogen physisorption, TPR, FT-IR and ICP-OES. High angles XRD patterns mainly reveals the formation of the corresponding oxides and, in a less extent, of the (phyllo)silicates for all monometallic samples. The (phyllo)silicates are responsible for the dispersion and stabilization of the resulted metallic active phases but also for the high reduction temperatures as observed in TPR curves. The TPR profiles display two maxima, the first one corresponding to the reduction of the metallic cation from oxides while the second one is attributed to the reduction of cations from (phyllo)silicates. The textural properties of the calcined catalysts are similar to those of the mesoporous SBA-15 support showing a narrow pore size distribution of the cylindrical pores. A new porous system is observed for Ni/ and Co/SBA-15 samples. The catalytic evaluation of the monometallic samples revealed a very active Ni/SBA-15 catalyst but less selective for CNOL. Co/SBA-15 converted only 18 mole % of CNA in 360 min of reaction but the selectivity to CNOL was much improved (60 mole % at $X_{CNA} = 20$ mole %). Cu/SBA-15 displayed no activity in the CNA hydrogenation.

Acknowledgement: *PNII-Idei, 264/2011 financed by UEFISCDI.*

Keywords: *mild drying impregnation; metal supported catalysts; hydrogenation; cinnamaldehyde;*

P-0671

BINOL AND SYNTHETIC BINOL DERIVATIVES AS POTENTIAL CHIRAL RESOLVING AGENTS

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BINOL was synthesized for the first time in 1926, but its ongoing interest as chiral inducer was only recognized after Noyori (Nobel Prize, 2001) discovered its application as ligand in the asymmetric catalytic reduction of aldehydes, in 1979[1]. Since then, the synthetic chemical modifications on BINOL molecule received enormous attention, mainly to obtain new chiral ligands for several asymmetric catalytic reactions[2].

BINOL was also recently described as an useful co-former for resolution of racemic mixtures by co-crystallization[3]. The use of stereoselective co-crystals represents an alternative strategy for chiral resolution, which is of particular relevance for substances which do not have the appropriate functional group to readily give rise to salts.

In this communication results on the investigation of the potential of BINOL and some synthetic BINOL derivatives as chiral resolving agents for selected chiral active pharmaceutical ingredients and diols are presented. Mixtures of the solid components, in different molar ratios, are submitted to mechanochemical methods which have proven to be an efficient method of co-crystal synthesis[4]. The outcomes of this process are evaluated by differential scanning calorimetry, polarized light thermomicroscopy and infrared spectroscopy.

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Keywords: *Binol; Co-crystal;*

P-0672

ROTATIONAL ECHO DOUBLE RESONANCE A VALUABLE TOOL TO INVESTIGATE THE SURFACE CHEMISTRY OF METAL NANOPARTICLES

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In the last decade the attention devoted to metal nanoparticles (MNPs) has been growing up rapidly, particularly due to their high application potential in colloidal and heterogeneous catalysis, i.e. hydrogenation, C-C coupling and oxidation reactions. The investigation of their surface chemistry is a crucial topic to understand the catalytic properties and to tune them up for technical reactions, as for example for Fischer-Tropsch, watergas-shift reaction, arene hydrogenation etc.

To characterize ligands, probe molecules or intermediates on the surface of MNPs solid-state NMR has been demonstrated to be one method of choice. It allows getting information about their location and dynamics which is important to understand their organization on the surface. In the present work the distance measurement between stabilizing ligands and carbon monoxide (CO) reactive molecules at the surface of phosphine-stabilized ruthenium nanoparticles (RuNPs) is demonstrated employing Rotational Echo Double Resonance (REDOR) experiments. The studied model systems are RuNPs in the size range 1-2 nm stabilized with 1,3,5-triaza-7-phosphaadamantane (PTA) or triphenylphosphine (PPh_3) ligands after exposure under CO atmosphere. This REDOR study sheds more light on interactions between reactive probe molecules and ligands as well as on their binding geometries at the surface and helps the interpretation of complex solid-state MAS NMR spectra of ligand stabilized RuNPs. Further, this study builds up the basis for advanced mechanistic investigations of complex MNPs systems.

Keywords: *NMR spectroscopy; Nanoparticles; Phosphane ligands; Surface Chemistry; Ruthenium;*

P-0673

ORGANIC SUPERCONDUCTING MATERIALS – RECENT RESULTS

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This work addresses the chemistry and selected physical properties of organic, super-conducting radical cation salts derived from bis(ethylenedithiolo)tetrathiafulvalene (BEDT-TTF or ET).

The following topics of general and recent interest will be highlighted in more detail:

Use of X-ray microcrystal diffraction and high resolution powder diffraction techniques for a better understanding of the properties of organic superconducting materials.

Organic superconductors under high pressure – crystallographic evidence for the existence of a new polymorphic phase of α-$(ET)_2I_3$ at high pressure.

Keywords: *superconductors;*

P-0674

ENTHALPY-ENTROPY COMPENSATION FOR N_2O AND CO ADSORPTION ON ZSM-5 CONTAINING TRANSITION METAL IONS

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The "enthalpy-entropy compensation" phenomenon refers to the linear scaling between enthalpy (ΔH) and entropy (ΔS) for a set of related reactions. At the "compensation temperature" any variation in enthalpy is balanced by such variation in entropy so that the total change in free energy remains constant[1].

There is a growing interest in manganese incorporation in zeolite lattices, mainly because of the role of this metal in numerous metallo-enzymes. Also, Mn^{2+} is a very active catalyst for SO_2 oxidation in aqueous phase.

In this work, thermodynamic parameters and the existence of enthalpy-entropy compensatory behaviour in adsorption of N_2O and CO on Mn^{2+} exchanged ZSM-5 zeolites, and bi-metallic FeMnZSM-5 and CuMnZSM-5 were investigated. The changes of entropy caused by N_2O and CO adsorption were calculated from differential heats [1].

The N_2O and CO adsorption was investigated by microcalorimetry and FTIR spectroscopy. Heats of adsorption were measured at 303 K in a heat-flow microcalorimeter (C80 Setaram) linked to a glass volumetric line. FTIR spectra were recorded using FTIR Brucker spectrometer with OPUS 22 software.

Existence of enthalpy-entropy compensation effect was evidenced by the linearity of –ΔH vs. –ΔS plots with the correlation coefficients 0.99, characteristic for all investigated zeolites, expect for CO adsorption on CuMnZSM-5. It was found that compensation effect depends on the type of charge-balancing cation. The compensation effect is governed by electrostatic interactions between highly polarizing cationic centres in zeolite and N_2O and CO molecules (depending of the size and charge of the cation) and by specific interactions (depending of the electron configuration of the cation).

Existence of the compensation effect is of interest for the possibility of predicting adsorption behaviour of the system and providing data for the zeolite as a catalyst.

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Keywords: *Adsorption; Zeolites; Thermodynamics;*

P-0675

STRUCTURE PREDICTION VIA AB INITIO ENERGY LANDSCAPES EXPLORATION OF GEF$_2$, A SYSTEM FEATURING LONE PAIR STRUCTURE CANDIDATES

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Predicting which crystalline modifications can exist in a chemical system requires the global exploration of its energy landscape.[1] However, the large computational effort involved in such global searches has required the use of a variety of empirical potentials and cost functions followed by a local optimization on the ab initio level. But this approach fails when systems are studied that exhibit unusual bonding situations such as mixed covalent-ionic bonding or sterically active inert electron pairs. In order to address this problem, one must employ ab initio energy functions already during the global optimization phase of the structure prediction.[2]

Germanium difluoride being such a system, we have studied its ab initio energy landscape using simulated annealing as a global exploration tool.[3] Most of the minimum configurations found during the global search exhibit structures with first coordination spheres that are characteristically unsymmetric, indicating a stereochemically active lone pair. Furthermore, many display covalently bonded substructures that are held together by interchain van-der-Waals interactions and F-Ge donor-acceptor bonds. Among the structures found are the known experimentally observed one (α-GeF$_2$), and, furthermore, one which turned out to be the correct solution for the (at the time of this study) not-yet solved structure of the high-temperature phase β-GeF$_2$. Detailed studies of the electronic and structural properties on ab initio level show that the experimentally observed spectrum of distances could be qualitatively reproduced without any heuristic input.

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Keywords: *GeF2; ab initio energy landscape; stereochemically; active lone pairs;*

P-0676

PHOTOLUMINESCENCE PROPERTIES OF NOVEL IONIC SILICA NANOPARTICLE NETWORKS

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Novel hybrid materials ionic silica nanoparticle networks (ISNN) were synthesized. The efficient formation of this novel hybrid material allowed to process the material into monolithic gels or transparent films. The ISNN presented very interesting photoluminescence properties.

For the synthesis of those hybrid materials, silica nanoparticles with an average diameter of 16 nm were modified with N-(3-propyltrimethoxysilane)imidazole. These imidazole modified silica nanoparticles reacted with halogen functionalized linkers. The coupling reaction, between the modified nanoparticles and the linker molecules, is a nucleophilic substitution. This substitution can be considered as a “click-chemistry-like” reaction. The molecules used as linkers consists in aromatic or condensed aromatic compounds containing two opposite-standing CH$_2$Cl-groups, such as p-Dichloroxylene or 4,4'-Bis(chloromethyl)-1,1'biphenyl.

The photoluminescence measurements performed on the ISNN hybrid materials showed emission bands over a broad range in the visible region. The silica nanoparticles, as well as the imidazole or chloroalkyl modified silica nanoparticles are non luminescent. In the specific cases where the pure dichloro linkers were photoluminescent, their emission maximum occured at a different wavelength than for the corresponding hybrid material.

SAXS measurements (Small Angle X-Ray Scattering) indicated a short range order which was assumed of being the origin for the photoluminescence properties of these hybrid materials. The short range order in form of strong π-π stacking interactions in the hybrid material was investigated when observing emission wavelength shifts by changing the linker.

The measured quantum yields up to 80% making this ISNN extremely promising for photoluminescence applications.

Keywords: *Green chemistry; Ionic liquids; Luminescence; Silicates; Sol-Gel processes;*

P-0677

EFFECT OF HYDROXYL DENSITY ON CONDENSATION BEHAVIORS OF SELF-ASSEMBLED MONOLAYERS AND PERFORMANCE OF PENTACENE-BASE ORGANIC THIN-FILM TRANSISTORS

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A series of self-assembled monolayers (SAMs), comprising octadecyltrichlorosilane (ODTS), dodecyltrichlorosilane (DDTS), and hexamethyldisilazane (HMDS), were prepared to examine the effects of phase states and condensation behaviors of SAMs on the morphologies and performance of pentacene-based organic field-effect transistors (OFETs) by means of Fourier Transform Infrared (FT-IR) spectrometer, atomic force microscope (AFM), X-ray diffraction (XRD), and semiconductor parameter analyzer. Experimental results reveal that the treatment of SiO_2 substrates with O_2 plasma (denoted as O_2-SiO_2) and the preparation temperature of SAMs dramatically influence the morphologies of SAMs and the performance of corresponding pentacene-based (no purification) OFETs. When the SAMs were prepared at 30 °C, the OFET based on ODTS-treated O_2-SiO_2 substrate had the highest hole mobility, reaching as large as 1.15 $cm^2V^{-1}s^{-1}$, and an on/off current ratio in excess of 10^5; these values are both much larger than those of a device based on ODTS-modified SiO_2 substrates without O_2 plasma treatment and O_2-SiO_2 substrates modified by ODTS SAMs prepared at other temperatures. OFETs based on O_2-SiO_2 substrates that were modified by DDTS and HMDS SAMs prepared at 4 °C performed best.

Keywords: *Organic field-effect transistors; self-assembled monolayer; pentacene; O2 plasma; preparing temperature;*

P-0678

DEVELOPMENT OF WATER-BASED SOL-GEL COATINGS AS ADHESION PRE-TREATMENT FOR ALUMINIUM SHEETS

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Since 2000, as the chromate conversion coatings were forbidden in the automotive and aircraft sector, much research has been done to find a follow-up system for corrosion protection of aluminium. Sol-gel coatings are very promising because the precursors can be modified easily and the coatings can be tailored for different requirements.

This work deals with the development of water-based coatings providing a good pre-treatment for adhesive bonding as well a good corrosion protection, even after aging under corrosive conditions.

Based on a coating system which consists of zirconia nanoparticles embedded in a silica network[1] made of tetraethyl orthosilicate (TEOS) and glycidoxypropyltrimethoxysilane (GLYMO), a water-based coating was developed. Furthermore the replacement of zirconium by titanium was tested. This new system was varied with regard to the aging time of the sol, ratio of transition metal precursor and water proportion. The suitability as adhesion pre-treatment was tested by tensile shear strength measurements. Additionally, the aging resistance was investigated by storing the bonded specimens in a salt spray chamber for 480 hours and testing them after this treatment. Morphological characterization was done by SEM and the composition was investigated by XPS.

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Keywords: *Aluminum; Sol-gel processes; Water chemistry;*

P-0679

INVERSE GAS CHROMATOGRAPHY AS A VERSATILE TOOL FOR THE DETERMINATION OF PHYSICO-CHEMICAL PARAMETERS OF THE METAL-ORGANIC FRAMEWORK HKUST-1

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Metal organic frameworks (MOF) are highly porous hybrid compounds consisting of inorganic and organic building blocks, called secondary building units (SBU) and linker molecules. Since 1999, the year of the discovery of HKUST-1 and MOF-5, this field of research has constantly grown and very different fields of application, such as catalysis and gas storage, are explored.

In recent years several studies in the field of MOF-based gas chromatography demonstrated the potential of MOFs as stationary phases for so-called PLOT (**p**orous **l**ayer **o**pen **t**ubular) columns.[1] Beside its function as an analytical tool, MOF based stationary phases in gas chromatography offer a convenient tool to determine fundamental thermokinetic data for the interaction of a large number of volatile compounds with the respective MOF structure. Furthermore the investigation of kinetic and thermodynamic phenomena is one of the prerequisites in order to find new and optimized practical applications and to understand the specific properties of the MOF-materials in question.

Based on the analyses by Cremer, van Deemter, and Golay, adsorption enthalpies, entropies, diffusion constants and other parameters can simply be gained by retention time and peak shape measurements. Beside the interaction with simple hydrocarbons, we investigated the interaction of electron donating analytes, such as aromatic and free electron pair possessing compounds with HKUST-1 as a representative of MOFs with open metal sites by inverse gas chromatography.

In this contribution a new method preparing the corresponding MOF based PLOT capillary columns is also presented, called the cyclic CSA (Controlled SBU Approach) coating procedure.

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Keywords: *Metal-organic frameworks; Gas chromatography; Kinetics; Thermodynamics; Synthetic methods;*

P-0680

VISIBLE LIGHT REACTIVE PHOTOCATALYST N-DOPED TiO_2 SYNTHESIZED AT A LOW TEMPERATURE

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It is said that photocatalyst N-doped TiO_2 which is sintered at 400–500 °C has a highest catalytic activity. However, it is also said that in this temperature, reoxidation of catalyst causes the deterioration of activities. In this study, we attempted to synthesize N-doped TiO_2 at a lower temperature and evaluated the properties. The samples were prepared in the sol-gel method and fired at 300, 400 or 500 °C after mixed with urea. These samples were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), UV-vis diffuse reflectance spectroscopy (UV-vis DRS). The photocatalytic activity of the samples was determined in the methylene blue decomposition with 470 nm wave-length visible light. All samples had an anatase-type structure. The sample sintered at 500 °C had a highest crystalline. The sample prepared at 400 °C had a highest absorption of visible light. However, the sample which adsorbed and decomposed the methylene blue most efficiently was that one prepared at 300 °C. In the catalytic activity test of the gel precursor before calcination and non-doped TiO_2, it was observed that non-doped TiO_2 did not adsorb the methylene blue but gel precursor adsorbed it. Moreover, the adsorption of methylene blue of the sample after N-doping increased materially. These results mean that the sample which is doped nitrogen and has a low crystalline adsorbs the methylene blue efficiently. The most nitrogen was doped in the sample fired at 300 °C. The catalytic activity of this sample was about twice as high as that of one commercial available TiO_2 catalyst. It is believed that N2p orbitals were hybridized to the valence band in the catalyst and this caused the improvement of the hole mobility and quantum efficiency.

Keywords: *Solid-state structures; Synthetic methods;*

P-0681

TWO ISOESTRUCTURAL HYBRID COMPOUNDS BASED ON KEGGIN-TYPE POLYOXOMETALATES AND COPPER-PICOLINATE COMPLEXES

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Polyoxometalate chemistry is one of the many areas in inorganic chemistry that is developing most rapidly today driven by their versatile nature in terms of structure, size, redox chemistry, photochemistry, and charge distribution[1]. One of the most remarkable approaches in POM chemistry is the design of functionalized materials based on POMs and different transition-metal complexes[2]. Incorporation of metalorganic moieties into inorganic oxide clusters provides a powerful method for structural modification and synthesis of novel metalorganic-inorganic hybrid materials that combine the features of both substructures resulting in large numbers of one-, two- and three-dimensional compounds[3].

In this work we report the synthesis, chemical and spectroscopic characterization, X-ray structure and magnetic properties of two hybrid inorganic-metalorganic compounds based on Keggin type polyoxometalates as inorganic building block, which are decorated with a copper-picolinate metalorganic complex and guanidinium cations; $[C(NH_2)_3]_4[\{SiW_{12}O_{40}\}\{Cu(pic)_2\}].nH_2O$ and $[C(NH_2)_3]_4[\{GeW_{12}O_{40}\}\{Cu(pic)_2\}].nH_2O$. These compounds were both prepared by open air methods.

The structure of these compounds can be described as double layers of keggin-type polyanions joined together through hydrogen bonds involving guanidinium cations. These layers are joined together by π-π interactions of the picolinate rings creating a hydrophobic area. These layers are stacked along the z direction, following the sequence: $Cu(pic)_2$-[POM- Gua –POM] -$Cu(pic)_2$.

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Keywords: *polyoxometalate; keggin; copper-picolinate;*

P-0682

CORROSION-RESISTANT CERAMIC COATINGS FOR SOLID OXIDE FUEL CELL INTERCONNECTS

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Solid oxide fuel cells (SOFC) are environmentally friendly electrochemical devices, used to produce the electricity from gaseous fuels, such as hydrogen or methane. Each cell operates at high temperatures and uses a dense layer of solid oxide electrolyte to transport oxide ions between electrodes. Interconnects are current conductors that connect each cell in series. These materials separate the neighboring anode and cathode compartments of two adjacent cells. Interconnects need to be stable and corrosion-resistant at elevated temperatures. Candidate interconnect materials are ferritic steels since metals are less brittle, cheaper and easier to shape compared to traditional $LaCrO_3$-based materials. Nevertheless, metallic materials react with corrosive gases and form poorly conducting surface oxide layers. Corrosion resistance can be greatly improved by ceramic coating. The coating is an oxygen transport barrier. Furthermore, the coating material can be a source of metal cations, such as Mn^{3+}, Ti^{3+} and La^{3+}, which may improve the oxide scale conductivity and/or adhesion to the metal surface. In the present work, the corrosion resistance of candidate steels for SOFC interconnects is studied. The steel sheets were cut, ground and coated by a single and double layer ceramic coatings based on lanthanum strontium manganese oxide (LSM) and cobalt oxide. The samples were annealed for 140 – 1000 h at 1123 K in different oxidizing atmospheres. The corrosion kinetics was followed by measuring the mass increase of the samples over time. The oxide scale phase composition and microstructure are studied by XRD and SEM/EDS. The mass gain of the samples follows a parabolic rate law. The parabolic rate constant decreases with increasing chromium concentration in the steel. Furthermore, dense LSM and Co_3O_4 coating layers significantly reduce the oxidation rate. The reaction mechanism is proposed. The results are discussed in relation to the proper interconnect functioning in a working SOFC stack.

Keywords: *Fuel cells; Ceramics; Oxidation; Kinetics;*

P-0683

POLYMORPHISM OF TRANS-1,4-CYCLOHEXANEDIMETHANOL

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Cyclohexane derivatives, despite the simplicity of their molecular structures, show a complex solid state phase behaviour [1, 2]. One of the dihydroxylated derivatives, *trans*-1,4-cyclohexanediol, has the particularity of presenting in the crystal lattice of the two known polymorphs bi-equatorial conformers as well as conformers in which the hydroxyl groups have the axial-axial orientation[3, 4]. 1,4-cyclohexanedimethanol differs from 1,4-cyclohexanediol only in two methylene groups placed between a cyclohexane carbon atom and the OH group, which may confer more flexibility to the molecule. This study aims to investigate the polymorphism of 1,4-cyclohexanedimethanol and to evaluate the influence of the substituent group in the stabilization of the axial conformers.

Trans-1,4-cyclohexanedimethanol polymorphic forms were generated by crystallization from solutions, and by cooling the melt. A combined approach using differential scanning calorimetry, polarized light thermomicroscopy and X-ray diffraction has been employed in the results interpretation. Two polymorphs were isolated and their crystal structures were solved by single crystal X-ray diffraction, at room temperature**.**

The conformational space of *trans*-1,4-cyclohexanedimethanol was studied by computational calculations at the MP2 level of theory, investigating the relative stability of the different equatorial and axial conformers. The comparison of the most stable structures for the isolated molecules and in the crystal will permit to draw insight on the relative importance of the molecular stability and intermolecular association in order to explain the conformational preferences of *trans*-1,4-cyclohexanedimethanol.

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Keywords: *Polymorphism; Crystal growth; Calorimetry; Conformation analysis; X-ray diffraction;*

P-0684

THERMAL BEHAVIOR OF CANDESARTAN CILEXETIL COMPLEXES

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A lot of newly developed pharmaceuticals are poorly soluble drugs.[1] This project deals with improvement of candesartan cilexetil solubility. Candesartan cilexetil is very poorly soluble antihypertensive drug. It is a prodrug of candesartan exactly, which selectively affects secreting of angiotensin II, the main generator of hypertension.

The major goal of this project is to test improvement of candesartan cilexetil solubility using different types of cyclodextrin (β-cyclodextrin, hydroxyl-propyl-β-cyclodextrin, sulphated-β-cyclodextrin and carboxy-methyl-β-cyclodextrin) and porous starch.[2-3]

We have used thermal analysis as a great tool to characterize complexes of candesartan cilexetil with cyclodextrins and systems with porous starch. This both groups are bonded with candesartan thanks to weak interactions, which effect synthesis of complexes and better soluble systems with candesartan cilexetil. Those are hard to characterize using other solid state analysis methods. By using DSC it is possible to distinguish complexes from simple mixtures of candesartan cilexetil with cyclodextrins and starch. Characterization of such complexes via thermal analysis and contribution to the candesartan solubility will be discussed.

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Keywords: *Cyclodextrins; Calorimetry; Drug delivery;*

P-0685

NANOENGINEERING BIOMIMETIC TiO_2-BASED PHOTOCATALYSTS FOR POLLUTION CONTROL FROM A DETAILED STRUCTURAL/MECHANISTIC UNDERSTANDING

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Biomimetic chemistry started in the realm of organic chemistry but has progressed to benefit materials design and now catalytic chemistry. With evolution many living plant and animal species have constructed species-specific biominerals/biocomposites that have nano-architectures that are the envy of materials scientists. Here we show how one can learn from and overcoat some of nature's 8.7 million biotemplates available on Earth with TiO_2-based phases to form novel hybrid nanostructures and then remove the biotemplate to produce novel intricate TiO_2-based replicas that show novel green photocatalytic properties in pollutant control.

TiO_2 is a well known effective photocatalyst. It can be improved by an adsorbed dye sensitizer, Pt, ion-doping, lowering its particle size or changing the anatse:rutile ratio, but 100-120 nm thick anatase overlayers grown on rutile produce hetero-junctions exhibited even higher pseudo-first-order rate constants and rates of photocatalysed dye decoloration. Since TiO_2 photocatalytic properties are structure-dependent, new and interesting properties were expected from the unusual and complex biomimetic TiO_2-based replica structures. This is the focus of the present work.

The photocatalytic activities and selectivities of the biomimetic TiO_2–based material coatings in the control air pollutant (toluene, HCHO, NO_x) and water pollutant (0.1mM methyl orange, benzene, toluene, phenol, alkyl phenol and alkyl phenol ethoxylates) levels per unit area were found to be much higher than those of commercial TiO_2 nanoparticulate coatings using a 0.5kW photon source. The modes of action of these biomimetic photocatalysts were investigated in-situ by FTIR-UV-vis-RGA analysis. Doping (e.g. Eu^{3+}) allows the biomimetic catalyst fine-tuning.

The potential of this approach for improved green catalysts in general (and TiO_2 photoanodes in DSSCs [30], photocatalysts for CO_2 reduction and water splitting and *metal* fuel cell electrodes and antibacterial coatings) is considered in detail.

P-0686

INFLUENCE OF HEAT TREATMENT ON STRUCTURE OF ELECTROPLATED PD-NI-P METALLIC GLASS FILMS

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The metallic glass is amorphous alloy with a glass transition temperature and supercooled liquid region. It is possible to give the material the new function, when various material surfaces are coated with such metallic glass film. Though the producing of the amorphous alloy by the electrodeposition is well known, the report on the electrodeposition of metallic glass film is not found except our papers. We have investigated the formation of Pd-Ni-P metallic glass films using the electrodeposition method from the view point of the bulk Pd based metal glass studied in great numbers as a basic research material.

In this study, the influence of heat treatments at the temperatures of supercooled liquid region on the crystal growth was examined in the electroplated Pd-Ni-P metallic glass film having various composition.

The substrates were sheets of Cu and Ti with dimensions of 15 x 67 x 0.20 mm. The base composition of electrolyte for Pd-Ni-P electroplating was $PdCl_2$, $NiSO_4$, H_3PO_4, $NH_2CH_2CH_2NH_2$ and NaCl. Heat treatments of the electroplated films were carried out using an infrared gold image furnace (MILA-3000, ULVAC) under Ar gas atmosphere. The films were characterized by X-ray fluorescence analysis (XRF), X-ray diffraction (XRD) and differential scanning calorimetry (DSC).

The glass transition temperature and crystallization temperature of the electroplated $Pd_{44}Ni_{38}P_{18}$ metallic glass film were 571 K and 646 K, respectively. XRD examination for $Pd_{44}Ni_{38}P_{18}$ metallic glass film shows that the pattern consists only of one broad peak and no distinct crystalline peaks can be seen from the films formed by electrodeposition, indicating that there exists an amorphous metal. After annealing at the temperature over 603 K for 30 min, some crystalline peaks, which are attributed to Pd, Pd_5P_2, Ni_3P and Ni_2Pd_2P, were observed at the XRD patterns.

Keywords: *Heat treatment; Electroplating; Pd-Ni-P; Metallic glass; Crystallization;*

P-0687

GE-GA-SB-S AMORPHOUS CHALCOGENIDES DOPED WITH RARE-EARTH ELEMENTS

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Amorphous chalcogenides are very promising materials for various applications in infrared spectral region because they have a broad optical window from visible to mid-infrared spectral range, a high refractive index, low phonon energy and some of them are photosensitive. These properties predetermine them for using as host matrix materials for doping with rare-earths elements[1, 2].

Nowadays the renewable energy sources are in the spotlight. Our work is focused for preparation of photon up-converters which can be used for enhancement of silicon solar cell efficiency as well as for telecommunications.

Various compositions of Ge-Ga-Sb-S amorphous chalcogenides were prepared by the conventional melting-quenching technique in sealed silica tubes from pure elements. Some of these materials were used for deposition of films onto microscopic glassy substrates by pulsed laser deposition and flash thermal evaporation techniques. The chemical composition of prepared samples was investigated by EDX spectroscopy, their crystallinity by XRD analysis. Variable angle spectroscopic ellipsometry was used for determination of the optical band gap energy, dispersion of the refractive index, thickness and roughness of films and for study of optical homogeneity. Up-conversion and photoluminescent spectra were studied via photoluminescence spectroscopy with using of tunable Ti:sapphire laser as excitation source. The results are discussed.

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Keywords: *chalcogenides; rare earths; up-conversion; luminescence; Ga-Ge-Sb-S;*

P-0688

EXPLORING THE STRUCTURAL ENERGY LANDSCAPE OF ULTRA MICROPOROUS FRAMEWORK MATERIALS

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Materials with molecular-scale porosity are important in wide range of applications such as gas storage, molecular separation, and heterogeneous catalysis. Framework materials offer scope for ultra high porosities and hence high gas uptake values.

The structural properties of a polymer can have a direct influence over its ability to pack efficiently and hence direct void formation and connectivity. For example, the series of conjugated microporous polymers (CMPs) show statistical control over the pore dimensions and surface area by systematically changing the length of the strut and the node topology.[1] Porous aromatic frameworks (PAFs) were recently discovered and showed ultra high surface areas (SA_{BET} 5600 m^2/g). A highly crystalline diamondoid topology was suggested as a structural model. However, the PXRD suggests an amorphous structure and an alternative structure based on the amorphous structure of silica has been suggested.[2] However, the calculated surface area for this model does not exhibit the ultra high surface areas observed experimentally.

The energy landscape of the range of possible structural models available has been explored by mapping the PAF-1 node-strut structure onto a series of amorphous and crystalline silica topologies. Gaining a structural understanding of the PAF-1 system may open pathways to designing novel ultra porous materials.

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Keywords: *Microporous materials; Amorphous materials; Solid state structures; Computational Chemistry;*

P-0689

BIMETALLIC NICU NANOPARTICLES CONFINED IN THE MESOPORES OF SBA-15 AS EFFECTIVE CATALYSTS IN THE HYDROGENATION OF CINNAMALDEHYDE

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Bimetallic nanoparticles (NPs) confined within mesoporous host structures are emerging as very interesting materials for catalysis because: ***(i)*** as compared with the corresponding monometallic NPs, they have improved catalytic performances due to a synergy between the two metals, and ***(ii)*** they are highly sintering-resistant due to the geometric stabilization of NPs inside the host mesochannels. A novel mild drying impregnation approach was developed to successfully prepare bimetallic NiCu rod-like NPs confined within the mesopores of SBA-15 silica (S) (constant metal loading: 5 wt. %, variable *Ni/Cu* weight ratios: *4/1*, *3/2*, *2/3* and *1/4*), as shown by low- and high-angle XRD, nitrogen adsorption/desorption and TEM-EDX. It was observed that at similar particle size, the composition of bimetallic NPs determines to a large extent both the reducibility and catalytic performance in the hydrogenation of cinnamaldehyde (CNA). Hence, characterization by H_2-TPR revealed an optimal reducibility at Ni/Cu ratios of *3/2* and *2/3*(T_{red} ~ 180-240 °C), which is much improved when compared with monometallic Ni/S and Cu/S reference samples (T_{red} ~ 510 and 345 °C, respectively). This is best explained through the existence of strong Ni?Cu interactions in the bimetallic nanoparticles. The catalytic results showed an outstanding catalytic activity of the bimetallic NiCu/S-*4/1* catalyst when compared with either Ni/S or Cu/S (initial reaction rates of 3.212, 1.909 and 0.008 $\mu mol_{CNA} \cdot g_{cat}^{-1} . s^{-1}$, respectively). As a general trend, the gradual decrease of the Ni/Cu ratio is followed by a decrease in the catalytic activity of bimetallic catalysts. Interestingly, the selectivity to cinnamyl alcohol (measured at X_{CNA} of 20 mol %) continuously increased from 1-2 mol % (Ni/S) up to 15-16 mol % (NiCu/S-*1/4*), suggesting that the gradual addition of inert Cu to active Ni causes changes of its geometric and/or electronic properties, which finally results in enhanced chemoselectivity of NiCu/SBA-15 catalysts.

Acknowledgement: *PNII-Idei, 264/2011 financed by UEFISCDI.*

Keywords: *Supported catalysts; Nanoparticles; Metals; Mesoporous materials; Hydrogenation;*

P-0690

CHARACTERIZATION OF COBALT BASED TPP-BIPY COORDINATION POLYMER

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Metalloporphyrin systems are one of the cornerstones on which the existence of life is based, as major biochemical, enzymatic and photochemical functions depend on the special properties of the tetrapyrrolic macrocycle.[1] The possibility of introducing porphyrin units into MOFs (metal-organic frameworks) increases the variety of new materials based on these macrocycles. During the last years, cobalt porphyrins are well-known to be prominent catalysts for oxygen reduction reactions (ORR)[2] and in order to obtain materials which provide new properties our research group is working with different combinations of metalloporphyrins and organic ligands .[3]

The work herein presented aims to the characterization of $[CoTPP(bipy)] \cdot [CoTPP]_{0.22} \cdot TPP_{0.78}$ (TPP = *meso*-tetraphenylporphyrin and bipy = 4,4'-bipyridine) compound in order to know the thermal, electronic and catalytic properties of these new porphyrin-based coordination polymer.

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Keywords: *Porphyrin; Metal-organic frameworks;*

P-0691

MOLECULAR INTERACTIONS IN COMPLEXES OF 4,4'-DINITROBIPHENYL

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The focus of this study was to investigate the nature of molecular donor-acceptor interactions in the solid state, using spectroscopic techniques such as IR, Raman, NMR and X-ray crystallography. Complexes of para disubstituted and 4-monosubstituted biphenyl formed with 4,4'-dinitrobiphenyl (DNBP), demonstrate intense colours upon formation, dissimilar to the colour combination of the parent compounds. Typical interactions observed in such molecular complexes include pi-pi interactions, hydrogen bonding, charge transfer and van der Waals interactions. Complexes of DNBP, as the host molecule, included a variety of mono- and disubstituted biphenyl donors or guests, such as dihalo, diamino, di- and monohydroxy groups[1], as well as urea with a 1:1 host:guest ratio[2] and thiourea with a 7:6 ratio. Molecular complexes formed between DNBP with difluorobiphenyl with a 3:1 ratio and DNBP with dibromobiphenyl and diiodobiphenyl with 4:1 ratios. The crystal structures of these complexes showed retention of the non-planar conformation of DNBP with a dihedral angle between the phenyl rings of around 35° [3].

The conformation for DNBP has also been studied using density functional theory (Guassian03) calculations that showed good agreement between the theoretically calculated and experimentally observed IR and Raman spectra in the solid state. The packing of the complexes in the solid state is directed mainly by the similar packing of DNBP units in these complexes. Some of the molecular ratios for these complexes that vary, depending on the electronic properties of the donor molecules, were determined using NMR spectroscopy.

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Keywords: *Host-guess systems; X-ray diffraction; computational chemistry; Density functional calculations; Charge transfer;*

P-0692

INFLUENCE OF WATER/ETHANOL RATIO IN SYNTHESIS OF N, S DOPED TIO2 ON PHOTOCATALYTIC ACTIVITY

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In this study, visible light reactive N-doped and N, S co-doped TiO_2 sample were prepared in the sol-gel method and sintered after mixed with urea or thiourea. These samples were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), UV-vis diffuse reflectance spectroscopy (UV-vis DRS). The photocatalytic activity of the samples was determined in the methylene blue decomposition. In the synthesis of N-doped TiO_2, the specific surface area of precursor was increased with decreasing the water/alcohol ratio in the hydrolysis reaction. However, the samples prepared by the higher alcohol quantity had the lower visible light absorption because of the reoxidation in the calcination. The sample with sulfuric acid treatment before recalcination could be controlled the absorption of visible light because of the restraint of reoxidation by sulfuric acid on the surface of the sample. On the other hand, in XPS result of the sample prepared by thiourea, the peak identified as S^{6+} which was derived from sulfuric acid was observed on the surface of the sample. The peak intensity of N^{3+} was increased and that of S^{2-} was decreased in the bulk of sample with increasing the quantity of water. The absorption of visible light was decreased with increasing the water supply. The case that N^{3-} is doped in O^{2-} site needs oxygen defect in order to compensate the electric charge. These defects increase the recombination center. However the dopes of S^{2-} do not cause the oxygen defects. This means that TiO_2photocatalyst doped S^{2-} is more effectual than that doped N^{3-} on the methylene blue decomposition and it is possible to control of dopant quantity by the water addition ratio. In this study, we could not confirm the effect of co-dope.

Keywords: *Titaniumu dioxide photocatalyst; N, S co-doping; water-adding quantity;*

P-0693

HYDROTHERMALLY SYNTHESIZED NANO-$CE_2SN_2O_7$ VIA [BMIM][CL] AND DTAB WITH PHOTOCATALYTIC PROPERTY

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In recent years, a lot of research has been extensively investigated to manufacture nanoscaled materials in order to create numerous properties in them. These are of interest for potential technological and medical applications. Today the hydrothermal technique is easy and effective, method with high reproducibility and good control over the composition and morphology of nanocompounds. One kind of these nanocompounds is nanosize semiconductors. A variety of semiconductor materials such as oxides and sulfides act as photocatalysts and degrade toxic organic compounds, dyes and others contaminants in wastewater[1].

In current research, synthesis of $Ce_2Sn_2O_7$ nanocomposite has been discussed by $SnCl_4.5H_2O$ and $Ce(NO_3)_3$ (1:1). pH of the media was gradually adjusted with sodium hydroxide. Then, addition of [bmim] [Cl] and DTAB was separately carried out to the previous solution. All of the reactions were done under N2 gas. Two homogeneous solutions were transferred into autoclaves and heated at 180–200 ºC in different times. Two obtained precipitates were separated by centrifuge, washed with water and dried in vacuum oven. Surfactant and ionic liquid were eliminated by calcination and washing respectively. The final products were characterized by XRD, FT-IR, SEM and EDX. The obtained results comparison of two methods showed figure of the nanocomposites are different within two methods. Therefore surfactant and ionic liquid are important and give effect to figure of the nanocomposites.

Also, these products were used to remove different kinds of textile dyes from industrial wastewater. Photocatalytic degradation experiments were investigated under sun light and ultraviolet irradiations for both of the products and the results were compared to gather.

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Keywords: *nanocomposite; hydrothermal synthesis; photocatalytic property;*

P-0694

CONTROLLED FORMING OF AGCL NANOSTRUCTURES ON AGBR NANOCRYSTAL SURFACE

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Ag-containing nanomaterials are used in many catalysis areas. Their creation may be based on the photographic processes, for example, by means of the formation of AgBr nanocrystals having a desirable form and size. For this purpose the controllable two-jet crystallization method is used, it consists in simultaneous addition of KBr and $AgNO_3$ with certain concentrations at a constant rate into the solution whose temperature is kept constant. It enables us to prepare the substrate which contains homogeneous tabular AgBr nanocrystals with the thicknesses ~100 nm.

The catalysis properties of the initial nanocrystals may be changed by means of the formation of the heterocontact structures on the surface of the initial AgBr nanocrystals. These structures are AgCl nanocrystals, i.e. epitaxial particles. They was synthesized in two ways: by adding KCl and $AgNO_3$ solutions into the initial substrate under certain conditions (Method I), or, by adding the substrate containing previously synthesized AgCl nanocrystals into the initial substrate (Method II). The resulting epitaxial particles are located along the entire surface of the initial AgBr crystals.

The surfaces of the initial AgBr nanocrystals were varied by adding the surface modification agent KJ into the initial substrate. In this case the number and the location of epitaxial particles on the surfaces of AgBr nanocrystals depend on the concentration of the iodide ions. It is established that at a certain concentration of the surface modification agent, the epitaxial particles are formed only onto the corners of the modified AgBr nanocrystals (Method I) and onto their sides (Method II).

Photolysis and next chemical treatment of the substrate with the initial and modified AgBr nanocrystals results in the Ag-containing nanocrystals with different surface structures.

Keywords: *Silver bromide nanocrystal; Epitaxy; Nanostructure;*

P-0695

STEAM REFORMING OF METHANE OVER NICKEL CATALYSTS SUPPORTED ON NANOCRYSTALLINE MAGNESIUM OXIDE

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The conversion of methane to valuable chemicals is very important. In the past decades, the most studied technology for syngas production was steam-methane reforming (SMR), in which methane reacts with steam to produce a mixture of hydrogen, carbon dioxide, and carbon monoxide. In order to obtain acceptable reaction rates, a catalyst is required to accelerate the process. In this study, Ni catalysts supported on nanocrystalline magnesium oxide with high surface area and various Ni loadings (5, 7, 10, 15 wt%) have been employed in steam reforming of methane (SMR) and the effect of Ni loadings on the catalytic activity was investigated.

The preparation of MgO via surfactant-assisted precipitation method led to the formation of a nanocrystalline carrier for nickel catalysts. The synthesized samples were characterized by XRD, BET, and TPH techniques. The results showed that the prepared catalyst with 7 % Ni loading indicated high activity and good stability in steam reforming reaction. It could be attributed to high dispersion of reduced Ni species and basicity of support surface.

Methane conversions of 4 catalysts with different Ni loading were shown that the catalyst with 7% Ni loading has higher conversion at all temperatures. Specially, at higher temperatures, higher activity of 7%Ni/MgO catalyst is more distinguishable. However, if the Ni content is higher than 7 wt%, there is a negative effect on the catalytic activity of SRM over reduced Ni/MgO catalyst.

Keywords: *Nickel; nanostructures; Magnesium;*

P-0696

THE CHEMISTRY OF DISULFIDE-DECORATED MONOLAYER SURFACES

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The attachment of bio-molecules to surfaces is of considerable importance both in the study of their fundamental properties and mode of action and in the creation of devices based on molecular arrays for screening and sensing. Thiol-bearing SAMs provide a platform for a stable (covalent) anchoring of biomolecule in a well-defined orientation.

A possible surface anchoring strategy is to create disulfide linkages between surface thiols and those of the molecules to be immobilized. Surprisingly, disulfide anchoring is relatively uncommon and seems not to be able to achieve a high degree of loading of immobilized molecules on the surface.

The work reported herein describes the creation of uniform thiol-functionalized siloxane-anchored SAMs and their transformation into intra-monolayer (bridging) disulfides. These disulfides provide for the efficient immobilization of biomolecules bearing pendant thiols, with no need for added oxidant. A fundamental problem in developing this surface chemistry was the lack of analytical methods that distinguish between thiol and disulfide moieties on a surface. They have similar XPS binding energies and similar surface wetting properties, with no distinctive features in the routine FTIR window (4000-1500 cm^{-1}). Therefore, we also developed (and report herein) a method for distinguishing and quantifying thiol and disulfide surface functionality on a monolayer array. Our analysis is based on the reaction with 2,4-dinitrofluorobenzene (DNFB, Sanger's reagent). This reagent readily reacts with thiol-SAMs (but does not react with disulfides) to form stable derivatives with distinctive IR, UV, and XPS signatures.

P-0697

SELF-ASSEMBLED COMPLEXES OF QUANTUM DOTS AND ANTHRACENE DERIVATES

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Inorganic semiconductor nanocrystals known as quantum dots (QDs), owing to their peculiar photophysical properties, are emerging nanostructured materials that could find applications ranging from solar energy conversion to diagnostics and medicine. The particular property of these nanomaterials is their narrow emission band whose maximum wavelength can be precisely tuned by controlling the size of the nanocrystal.[1] Moreover, the broad absorption band in the UV-visible region, high absorption coefficient and high luminescence quantum yield, enable measurements of luminescence signal in extreme dilute conditions.

In this study we investigate the possibility of controlling and implementing specific physico-chemical properties by chemical functionalization of the QD surface. The surface of the nanocrystals can be decorated with organic molecules, via either covalent or non-covalent interactions. Based on previous work[2] we studied the association process of CdSe/ZnS core/shell QDs with an aminoanthracene derivative and with the corresponding ammonium species, which can be obtained by protonation of the former with an acid in solution. Our results show that both the QD luminescence and the anthracene fluorescence are quenched; moreover the emission intensity of the QD can be modulated by controlling the protonation state of the molecular species. This system could therefore be used as a luminescent pH sensor.

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Keywords: *Nanotechnology; Self-assembly; Luminescence; Quantum dots;*

P-0698

PHOTOINDUCED MEMORY EFFECT IN A REDOX CONTROLLABLE BISTABLE MECHANICAL MOLECULAR SWITCH

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A controllable molecular shuttle is a rotaxane that bears in the thread-like molecule (dumbbell) two or more units, whose affinity for the macrocycle can be tuned using external stimuli [1]. As result, the macrocycle can shuttle along the dumbbell.

In this work we present a study on a bistable molecular shuttle composed of cyclobis(paraquat-*p*-phenylene) (CBPQT, the ring) and a dumbbell-shaped molecule containing three functional unit: 1) a tetrathiafulvalene (TTF), 2) a dioxynaphtalene moiety (DNP) and 3) an azobenzene unit (AZO). TTF and DNP are two electron-donor units, that interact with the electron-acceptor CBPQT. AZO is a photocromic molecule that can be reversibly photoisomerized from its stable *trans* form to the metastable *cis* form. Initially the CBPQT is positioned on the TTF unit. After oxidation of the TTF unit, the CBPQT shuttles from TTF to the DNP unit across the *trans*-AZO. Upon UV irradiation, the AZO unit isomerizes from *trans* to *cis*. Reduction of the TTF^+ unit restores the initial situation under the electronic viewpoint but not for the conformational aspect: the rotaxane is locked in a metastable state where the CBPQT is forced to interact with DNP. The initial conformation is restored upon the thermal or photochemical *trans* to *cis*conversion of the AZO unit. Here we demonstrate the possibility to lock more than 50% of the rotaxane molecule in the metastable state[2]. This rotaxane is an example of flash memory where the written information is not erased after the removal of the writing stimulus.

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Keywords: *Rotaxanes; Molecular devices; Azo compounds; Nanotechnology; Supramolecular chemistry;*

P-0699

DONOR-ACCEPTOR PAIRS INCORPORATED IN NEW HYBRID MESOPOROUS SILICA NANOPARTICLES FOR SOLAR CELLS

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The morphology of the active layer in organic solar cells based on conjugated and small molecules (fullerenes or perylenediimides) plays a crucial role on the overall efficiency of the device. The poor compatibility between the two components, the nature of the solvent, and the conditions of wet-processing deposition lead to phase segregation with concomitant losses of energy, reductions on charge mobility transport and increase of the recombination process[1].

Mesoporous silica nanoparticles (MSNs) [2] with well-defined and controllable particle morphology are exceptional supports for molecules and polymers that have a tendency to aggregate or forming dimers with less desirable properties. Molecules with two or more trialkoxysilane groups can be incorporated in the silica framework during the synthesis of the nanoparticles, and the pore (after template removal) can accommodate polymers or other molecules.

The use of MSNs to incorporate donors and acceptors entities will maximize the interfacial area and the donor:acceptor contact increasing the active volume, and isolate the polymer chains into nanoscale domains leading to a confinement effect. This will control the phase segregation and minimize the recombination process, and improving charge separation and increase carrier's mobility.

Herein we present the preparation and photochemical characterization of hybrid MSNs incorporating perylenediimide derivatives in the walls and conjugated polymers on the pores. The photochemical and photophysical properties of these materials will give an indication about the most promising material for solar cells.

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Keywords: *perylenediimides; Mesoporous silica nanoparticles; Pedot; solar cells; Donor-Acceptor pairs;*

P-0700

DYNAMIC ANALYTE RECOGNITION BY ARTIFICIAL SYNTHETIC VESICLES

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Mimicking recognition processes at natural cell membranes we recently reported synthetic vesicles with multi-receptor surfaces as chemo sensors for small biomolecules.[1] Functional phospholipid-based membranes are used for optical sensing by fluorescent labelling of embedded molecules.[2]

To understand the physical interactions of vesicular anchored receptors we developed a simple model system for the dynamic recognition: multivalent target molecules spatially rearrange multiple membrane-embedded receptors equipped with FRET labels. These liposomal tethered amphiphiles are assumed to form patches and approximate with the addition of a binding partner to give a typical FRET response.

The influence of analyte binding towards the FRET signal was investigated by emission titrations. The investigation of these dynamic interactions is part of an approach towards imprinted vesicles as soft nanoparticles with ordered surfaces that perfectly match a templating target molecule.

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P-0701

CMOS-COMPATIBLE LOCALIZED GROWTH AND INTEGRATION OF SEMICONDUCTING NANOWIRES

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In recent years, one-dimensional semiconductor nanostructures with tunable morphologies, dimensions, crystallographic phases, and orientations have gained tremendous attention due to their vast number of applications, including electronics, sensing, energy harvesting, etc... Several techniques have been successfully employed for the growth of high quality semiconducting nanowires[1]; however, most of the processes using metal supported methodologies require high temperatures of an entire substrate for an effective formation of single crystalline nanowires.

In this study, we used micromembranes and microhotplates for the localized growth of high quality semiconducting nanowires, including Ge, SnO_2 and In_2O_3, via LPCVD techniques employing molecular sources. The heated areas were the range of several hundreds of square microns allowing a site-specific formation of nanowires. Key features of such microsystems are extremely fast cooling and heating processes due to their low mass and low power consumption. The growing nanowire bundles bridge the gap between a set of interdigital electrodes located on top of the heated membranes und thus leading to in situ contact formation. This approach allows us to perform heating and measuring operations independently, which is mandatory for thermally supported devices such as metal oxide gas sensors.[2] To the best of our knowledge, this is the first report for the growth of these materials using such a technique. Additional advantages include the possibility to grow various types of nanowires on the same chip using multiple micromembranes or microhotplates and the in situ contact formation replacing cost and time consuming procedures. The presented data will demonstrate the enormous potential of this approach for the fabrication of novel nanostructure-based devices.

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Keywords: *Chemical vapor deposition; Nanostructures; Nanotechnology; Sensors;*

P-0702

SYNTHESIS AND CHARACTERIZATION OF SIO_2-SUPPORTED FE/CO NANOPARTICLES

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Introduction of cheap, efficient and selective catalysts for production of fuels and heavier hydrocarbons from lighter ones is of great challenge in refineries and petrochemical industries[1]. Both Fe- and Co-based catalysts individually have advantages and disadvantages properties[2]. Therefore effort to couple them in the hope to bring forth a more efficient catalyst having parents' advantages is of great importance. Herein, a series of cobalt-iron nanocatalysts were prepared using some wet chemically methods and were characterized using thermal analysis (TGA/DSC), N_2 physisorption measurements such as BET, BJH, DH methods and X-ray diffraction (XRD) techniques. The average sizes of crystallites were determined below 100 nm from the half-width of the most intense peak of the diffraction pattern using the Scherrer equation. The crystallite sizes of catalysts were decreased with increasing SiO_2 content which clearly confirm. The Brunauer-Emmett-Teller surface area (BET SA) measures of the products show also that the increase of SiO_2 ratio results in an increase in the catalyst surface area linearly In the other hand, the pore volume increases with increasing of SiO_2 ratio to reach a maximum at 50% SiO_2, and then decreases with further increasing of SiO_2 ratio.

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Keywords: *X-ray diffraction; Iron; Cobalt; Sol-Gel Process;*

P-0703

RU(II) COMPLEXES ENCAPSULATION IN BIOCOMPATIBLE PLGA NANOPARTICLES – CHARACTERIZATIONS AND POTENTIALITIES IN TWO-PHOTON-PHOTODYNAMIC THERAPY

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Interest for nanoparticles in medicine (nanomedicine) was increasing the last ten years and especially as multifonctionnal compounds for imaging, diagnosis, and therapy. In this field, our team is engaged in the encapsulation of new coordination complex within biocompatible and biodegradable nanoparticles based on a co-polymer (PLGA) for applications in imaging, such as magnetic resonance imaging (MRI), or luminescence, and photodynamic therapy (PDT). In this context, the development of new Ru(II) complexes involving 1,10-phenanthroline-based ligands are developed. These compounds possess a wide 1MLCT-type absorption band around 450 nm, which makes them good candidates as sensitizers for the local photo-generation of cytotoxic singlet dioxygen1O2. Moreover, their third order nonlinear optical properties can be used in a two-photon absorption process. The optical properties and the potential in PDT (and two-photon-PDT, TP-PDT) of two ruthenium complexes (with different hydrophilic characteristics) and the related metalled nanoparticles [Ru]@PLGA are described and commented.

Keywords: *Ru(II) complexes; photodynamic therapy; nanoparticles; two-photon absorption; plga;*

P-0704

DENDRITIC POLYARILSILANES AS EFFECTIVE NANOSTRUCTURED LUMINOPHORES

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During the last years the number of light-harvesting luminescent dendrimers has increased rapidly. One of the most interesting features of dendrimers is a possibility of incorporation of different chromophores within one dendritic molecule that can lead to an intramolecular directional energy transfer from their peripheries to the centre (a molecular antenna effect). It allows tuning the emission color of the core across the entire visible spectrum, which provides an efficient tool for controlling a wavelength of light emission in organic photonic and electronic devices. Light-harvesting antennas are essential for natural photosynthetic processes and currently attracting much attention. Up to now different organic dendritic structures have been reported to show the antenna effect, but there are no organosilicon molecules among them, that is, containing thiophene and silicon units. It was recently shown that silicon atoms break the conjugation as well as increase the luminescence efficiency in bithiophenesilane dendrimers. In this work we report the synthesis and investigation of the organosilicone molecular antennas based on new oligoarylsilane compounds with different branching topology: dendrimers and "butterfly"-like molecules. Photoluminescence study of the new molecules has shown an intramolecular energy transfer with the efficiency up to 99% and luminescence quantum yield up to 87%.

We applied these molecular antennas as spectral shifters in new highly effective plastic scintillators (radiation detectors). Since two different luminophores are fixed properly on the nanoscale distance at the same branching molecule, both the light output and the attenuation length of the plastic scintillators significantly increase. This lead to a new type of scintillating devices with nanostructured luminophores.

Acknowledgement: *This work was supported by Foundation of President of the Russian Federation (project MK 1528.2011.3) and Presidium of Russian Academy of Sciences (Program No. 24)*

Keywords: *Dendrimers; Luminescence; Energy transfer; Nanostructures; Sensors;*

P-0705

NANOADHESION AND NANOFRICTION SURFACE PROPERTIES OF BIOPOLYMERS FILMS

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Hydroxypropyl methylcellulose (HPMC) constitutes one of the most dedicated polymers used in the production of film coatings for pharmaceutical applications (capsules, tablets,…).This study represents an attempt to assess adhesion and friction properties of such biopolymers at the nanoscale using the atomic force microscopy (AFM). Hydroxypropyl methylcellulose (HPMC) is a very important hydrophilic biopolymer for the preparation of oral controlled drug delivery systems due to its high swellability characteristic and film forming properties. Additives such as plasticizers, surfactants, lipids, colorants or other film-forming polymers are frequently incorporated into biopolymer matrices to produce high quality drug protective films and to control the surface sliding and adhesion properties. However, these additives do not affect only the bulk physicochemical properties of films, they also affect the surface properties. We point out the advantage of AFM and chemical force microscopy (CFM), based on force curve experiments, in the quantitative determination of the surface thermodynamic properties of biopolymer films, such as surface energy and thermodynamic work of adhesion. The study also concerns the interplay between nanoadhesion and nanofriction. The study investigates the influence of an hydrophilic plasticizer (polyol) and an hydrophobic excipient (fatty acid) on the surface properties of hydroxypropylmethylcellulose (HPMC) films. On the basis of original atomic force microscopy (AFM) experiments, interplay between nanoadhesion and nanofriction are detailed. The results clearly underline the strong dependence of film properties on additive nature, concentration or water sensitivity and the interplay with additive-biopolymer matrix compatibility. It also shows that first the HPMC-additive compatibility seems to be an interesting factor behind the variation of surface properties of HPMC formulated films, and second that formulation is an effective way to tune surface and nanoscale properties of HPMC biopolymer films.

Keywords: *Biopolymer; Atomic force microscopy (AFM); Nano-adhesion; Nano-friction; Cellulose-based polymer;*

P-0706

THE RELATIONSHIP BETWEEN THE PH INDUCED COLOR AND CONFORMATIONAL CHANGES IN YEAST CYTOCHROME C COATED GOLD NANOPARTICLES

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The uses of protein-coated metallic nanoparticles including gold as potential colorimetric biosensors and drug delivery vehicles have been studied extensively. A potential biosensor application for detecting protein folding/unfolding is yeast cytochrome c-coated gold nanoparticles. It was reported (Chah *et al*., Chem. Biol., 12, 323-328, 2005) cytochrome c-coated gold nanoparticles can be potentially used as a colorimetric biosensor for detecting acid-induced unfolding of cytochrome c, based on the observation of color changes associated with changes in pH, from neutral to acidic during this pH change; the color of a cytochrome c-coated gold nanoparticle suspension changes from red to blue and to clear.

In the present study, we comparatively analyzed the secondary structure of cytochrome c coated on different sizes of gold nanoparticles (13 nm and 19nm), and the unfolding at various pH conditions by FT-IR spectroscopy. The results of secondary structural analysis revealed that although the color changes coincided with the decrease in pH, as reported previously, this event is unrelated to the true acid-induced unfolding of the protein. The binding of cytochrome *c* to gold nanoparticles induces partial unfolding of the protein event at neutral pH condition. However, the unfolding of the protein does increase as pH decreases. The color changes are more related to the changes in sizes of gold nanoparticles due to aggregation than the acid-induced unfolding. By inserting a short linker molecule thiopropanonic ($HOOC(CH_2)_2SH$) between cytochrome *c* and gold nanoparticles (13 nm), the secondary structure of cytochrome c remains native at similar acidic conditions.

Keywords: *nanoparticles; cytochrome c; pH induced changes;*

P-0707

AMINO FUNCTIONALIZED IMIDAZOLIUM SALTS: DUAL ROLE PLAYERS IN ORGANOMETALLIC CHEMISTRY AND NANOSCIENCE

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Imidazolium salts incorporating functional groups on the cation and/or anion, represent a class of compounds having great versatility due to their applications as ionic liquids (ILs) or N-heterocyclic carbene precursors (NHCs). Our research in this field has been dealing with the synthesis of (Boc)-protected and deprotected amino-functionalized imidazolium cations $[NHR^1CH_2CH_2imR^2]^+$ ($[\mathbf{1}]^+$, R^1 = Boc, H; R^2 = Me, Bz, Trit) and related NHC-Ag(I) and Rh(I) complexes.[1] We have also demonstrated that $[NH_2CH_2CH_2imMe]^+$ plays a dual role in gold chemistry: **i***)* can give the gold(III)-aminoethyl imidazolium aurate salt $[Cl_3AuNH_2(CH_2)_2imMe)][AuCl_4]$ (**2**) used in the preparation of catalytically active gold nanoparticle-containing polycarbonate membranes or ITO glasses;[2] **ii)** can act as a primary amino-functionalized NHC precursor to give the dimeric, photoluminescent complex $[Au_2(NH_2(CH_2)_2imMe)_2][NO_3]_2$ (**3**).[3]

We now present some very recent results of a research focused on the preparation of detonation nanodiamond(ND)/Au_{NPs} hybrid materials. Two different experimental routes are followed for the decoration of ND by Au_{NPs}, that are in turn prepared by an innovative electroless approach using the gold complex **2**. Structure and morphology at the nanoscale level of the Au_{NPs}-on-ND deposits have been deeply investigated by electron microscopy (FE-SEM, HR-TEM) and diffraction (XRD) techniques. The optical properties of these systems have been determined by performing scattering and UV-Vis absorption measurements and by comparing the experimental data with simulated extinction spectra. The preliminary results of the present research establish the first rules for future designs of more complex Au_{NPs}/ND systems.

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Keywords: *Ionic liquids; Carbene ligands; Gold; Carbon; Nanostructures;*

P-0708

CHIRAL PORPHYRIN J-AGGREGATES INDUCED BY TARTARIC ACID

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Chirality expression in supramolecular assemblies is a very fascinating topic due to its close relationship with biological systems and the origin of life itself. Organization at higher levels is extremely intriguing in the case of achiral molecules that self-assemble in the presence of a chiral bias to afford chiral supramolecular complex structures. Chiral J-aggregates of the achiral $TPPS_4$ porphyrin represent a nice example that recently is gaining attention for their peculiar optical and structural features. The use of optically active tartaric acid as chiral inducer has been reported as the first example of organic aggregates showing magneto-chiral dichroism.[1] As part of our interest, we have also shown an interesting structural transition from fractal to rod-like aggregates, that depends on the porphyrin concentration and the ionic strength and that is responsible for a peculiar inversion of the circular dichroism spectra with the same templating enantiomer.[2] Chiral porphyrin nanoaggregates have been confined into microemulsions water pools achieving a remarkable scaling of the quality of the circular dichroism signal on the dimension from the nano- up to mesoscopic regime.[3] Here we report on the chiral induction mediated by D- and L- tartaric acid in bulk aqueous solutions. The kinetics of growth for chiral $TPPS_4$ J-aggregates induced by tartaric acid have been investigated under different experimental conditions.[4] We anticipate that, depending on the overall rate of the process, a distinctive kinetic difference, together with a variance in the extent of the chiral transfer, is clearly evident for the two enantiomeric.

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Keywords: *Aggregation; Kinetics; self-assembly; supramolecular chemistry; circular dichroism;*

P-0709

POLYOXOMETALATE RICH THIN FILMS WITH CONTROLLED STRUCTURE AND FUNCTION FOR DESIGNER ELECTRONICS

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During the last two decades, polyoxometalates (POMs) have attracted growing attention due to their potential application as functional materials potentially enabling new device design and opening new areas of technology. POMs are metal-oxide clusters of early transition metals Mo, W, V, etc with a diverse range of structures and properties, such as reversible electrical capacitance,[1] programmable surface 0D, 2D or 3D structure[2] which could together be of potential application in ultra-high-density data storage,[3, 5] catalysis[4] and also in medicine as antiviral drugs.[5] In the present work, we show that it is possible to assemble structured thin-films by the self-assembly/organization of different POMs (Mo96- and V16-clusters, TRIS-Mn-Anderson and Mn-Dawson types) onto solid supports via electrochemical co-deposition or by preparing multi-planar heterojunction structures with polymers via Langmuir-Schaefer deposition. In the framework of nanoscale organic/hybrid electronics we show here the relationships between the thin film structure and electrochromic or smart dielectric properties.

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Keywords: *Nanotechnolgy; Thin Films; Electrochemistry; Material Science; Self-Assembly;*

P-0710

SYNTHESIS OF MONODISPERSE CUSIO$_3$ HIERARCHICAL HOLLOW SPHERES (HHSS) AND THEIR SUBSEQUENT CONVERSION TO CU$_3$N/SIO$_2$ AND CUS/SIO$_2$ HYBRID HHSS

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Monodisperse hollow spheres are of great interest due to their characteristic shape, well-controlled size, high surface area and large void space, which makes them potential candidate for various technological applications. Inorganic silica-based composite materials having structural features in the nanometer regime are an important class of hybrid materials. The chemical inertness, high temperature stability and biocompatibility are important features of silica which makes them ideal constituent of nanocomposites. Exploring new morphologies of metal nitride and metal sulphide based nanomaterials, may deliver new or improved physical and chemical properties to meet the demands of future advanced functional materials.

$CuSiO_3$ HHSs were synthesized under hydrothermal conditions using monodispersed Stöber silica spheres as a chemical template[1]. A subsequent thermal treatment under ammonia atmosphere allowed formation of Cu_3N/SiO_2 hybrid HHSs. Furthermore, room temperature sulphidation reaction of $CuSiO_3 \cdot H_2O$ HHSs with aqueous $(NH_4)_2S$ gave CuS/SiO_2 hybrid HHSs. The Cu_3N/SiO_2 and CuS/SiO_2 hybrid HHSs were characterized by X-ray diffraction, transmission electron microscopy and energy-dispersive X-ray spectroscopy analysis. The morphology of $CuSiO_3 \cdot H_2O$ HHSs is well kept after nitridation and sulphidation reactions. The use of Stöber silica spheres as a chemical template appears to be a simple way to accomplish synthesis of monodisperse Cu_3N/SiO_2 and CuS/SiO_2 hybrid HHSs.

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Keywords: *Nanostructures; Silicates; Nitrides;*

P-0711

PREPARATION OF SUPRAMOLECULAR NETWORKS USING LANGMUIR-BLODGETT TECHNIQUES

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The liquid-air interface is an ideal environment for the preparation of monolayer regular grids using supramolecular (non-covalent) interactions that permit self-correction of errors. Connector molecules with polygonal shapes are deposited on the liquid surface and compressed to a desired area per molecule using a Langmuir-Blodgett trough, permitting hydrogen-bonding or metal ion-ligand interactions to occur. Hydrogen-bonded monolayers of the annulene derivative 2,2',2"-(1,3,8,10,15,17-Hexaoxo-5,6,12,13,19,20-hexadehydro--8,10,15,17-tetrahydro-1H-cyclododeca[1,12-*f*:4,5-*f'*:8,9-*f''*]--triisoindole-2,9,16(3H)-triyl)triacetic Acid [1] were formed spontaneously and were subsequently transferred onto various substrates and examined using UV/Vis, IR and STM techniques.

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Keywords: *Supramolecular; Monolayer; Langmuir-Blodgett;*

P-0712

INVESTIGATIONS OF NANOSCALE CARBAZOLE BASED ARCHITECTURES

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Massive fully conjugated cyclic π-systems are expected to show unique optical and magnetic properties, especially when the induced electronic coupling through the cycle is particularly strong.[1] Cyclic forms of linear chains can show marked differences in their photo-physical properties.[2] Carbazoles in particular are highly luminescent and as they are strong hole transporters, they are widely applied in opto-electronic devices and as such should prove ideal candidates for study. However carbazole based macrocycles reported to date lack efficient π-conjugation throughout their entire backbone.

Here we present the synthesis and physical investigations of model systems that maximise the conjugation in carbazole oligo-phenyl-ethylene rods and cycles. After establishing new synthetic routes towards carbazole based oligomers, we present a 26 step, template directed synthesis of a fully conjugated 7 nm diameter carbazole based macrocycle. A range of polar, orthogonal acetylene protecting groups were employed to assemble the macrocyclic structure via palladium catalysed cross-coupling reactions.[3] The carbazole moieties allow insertion of a semi-rigid template, facilitating an efficient cyclisation.

While studying the effect of substituent architecture and push-pull substituents in carbazoles we confirmed that 2,7-substituted carbazoles show considerably enhanced conjugation over other substitution patterns. Photo-luminescent studies showed that a bathochromic shift in absorption of the carbazole band of over 100 nm could be achieved in the monomer unit. Aggregation of short chain 9-substiuted carbazole could be studied by NMR, while further altering the 9-position lead to liquid crystalline behaviour.

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Keywords: *Alkynes; C-C Coupling; Donor-acceptor systems; Macrocycles; Supramolecular chemistry;*

P-0713

THE PECULIARITIES OF ME/NANODIAMOND CATALYSTS IN ETHANOL STEAM REFORMING FOR CO-FREE HYDROGEN PRODUCTION

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The study of ethanol steam reforming (ESR) in catalytic membrane reactors now attracts a great interest due to the possibility of manufacture of ultra pure hydrogen from accessible and renewable sources. The variety of heterogeneous catalysts of this process was offered, e.g., Rh, Ru, Pd, Pt and Ni on oxide supports. The problem of such systems is the catalyst deactivation because of carbon deposit formation during the process. The new carbon materials as catalyst's support may solve this problem due to their resistance to carbonization, high specific area and stability. Thus, nanodiamonds, produced by detonation synthesis (DND), are promising supports for platinum group catalysts due to similar lattice types of diamond and platinum metals and facilitated adhesion of the active metal to the surface of DND particles.

In this study the new catalysts of ESR were developed presenting Pt, Ru, Ni, Pt-Ni and Pt-Ru nanoparticles, supported on DND and prepared by IR-pyrolysis of precursors, based on metal salts and DND particles. The structure, phase content and morphology of obtained catalysts were determined by XRD, IR-spectroscopy and TEM.

ESR on powder metal-DND catalysts was carried out in conventional tube reactor (TR) at the temperatures from 300 to 550°C and the various water/alcohol ratios. The catalysts studied demonstrated high hydrogen productivity and stable activity during experimental tests. The individual Pt-, Ru- and Ni/DND catalysts had shown lower activity than bimetallic Pt-Ru/DND and Pt-Ni/DND catalysts. The highest hydrogen productivity and the lowest CO yield were observed on the Pt-Ru/DND catalyst.

ESR was carried out also in a plug flow membrane reactor with catalyst's fixed bed (MR) and membrane of Pd-Ru foil. Up to 18.2 mmol/g cat·h of ultra pure hydrogen was produced in MR with Pt-Ru /DND catalyst at the hydrogen recovery of 60%.

Keywords: *nanodiamond; catalyst; ethanol; reforming; membrane reactor;*

P-0714

PREPARATION OF RE-CRYSTALLIZED SILVER NANOPARTICLES VIA HIGHLY CONCENTRATED NACL SOLUTION FOR SURFACE ENHANCED RAMAN SPECTROSCOPY

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Since Fleishman's discovery in 1974 and Creighton rediscovery in 1977, surface enhanced Raman spectroscopy (SERS) technique has gained broad focus from scientists. SERS is a powerful tool for the study of single molecules in concentrations reached up 8 x 10^{-14} M. It is known that silver nanoparticles due to their unique optical properties served as the commonly used enhancers of Raman signal. An enhancement effect depends on the size and morphology of silver nanoparticles. For the ordinarily used argon laser with an excitation wavelength of 514.5 nm was observed to the 'hot particle size' ranging from 80 nm to 100 nm[1, 2].

This work presents the activation of silver nanoparticles for SERS measurements with excitation wavelengths both in the visible (488 nm) and near infrared region (1064 nm). The silver nanoparticles with an average particle size of 28 nm were synthesized by a reduction of silver ammonia complex by D-maltose and as activation agent of primary silver nanoparticles were used chloride anions with final concentrations of 400 mM. Particle size distribution measurements discover rapid recrystallization of primarily prepared silver nanoparticles to one-order larger crystallites (400 nm) appearing during 15 minutes from the moment of NaCl addition. It was proved, that recrystallized silver nanoparticles are efficient enhancers of Raman signal of both visible (488 nm) and near infrared laser excitation (1064 nm) as was observed in the representative spectra of adenine.

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Keywords: *silver nanoparticles; Raman spectroscopy; aggregation;*

P-0715

STRAIGHTFORWARD SYNTHESIS OF GOLD NANOPARTICLES SUPPORTED ON COMMERCIAL SILICA-POLYETILENIMINE BEADS AND THEIR CATALYTIC ACTIVITY

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Nanoscience and nanotechnology play an important role in the design of novel heterogeneous catalysts.[1] When the sizes of supported or unsupported metal particles are decreased down to a few nanometers, those metal nanoparticles (M_{NPs}) may exhibit unprecedented physicochemical and catalytic properties, not observed in bulk materials or large-sized particles. The nanoparticle sizes influence the surface-to-volume ratio and the surface energy of these materials, enabling to make them very active species in catalysis but, on the other hand, their stability decreases when they become prone to aggregation. To overcome this drawback, catalytic nanoparticles are hence usually immobilized on a suitable support material that also facilitates catalyst recycling.[2]

This study entails the synthesis and characterization of supported gold nanoparticles (Au_{NPs}) adsorbed on commercial polyetilenimine-functionalized silica beads (SiO_2-PEI) exploitable for heterogeneous catalysis. The Au_{NPs}/SiO_2-PEI catalysts were prepared by in situ postdepositon reduction of $HAuCl_4$ to Au(0) by the PEI itself, without the need of neither external reducing nor stabilizing agents.[3]

Six different types of Au_{NPs}/SiO_2-PEI were obtained and fully characterized by UV-Vis-DRS, XRF, SEM-FEG, XANES and EXAFS, more over the catalytic activity was evaluated for the reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) obtaining results in line with literature data.[4]

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Keywords: *gold; Nanoparticles; Heterogeneous catalysis; EXAFS spectroscopy; X-ray absorption spectroscopy;*

P-0716

FLUORINATED ORMOSIL NANOCAPSULES AS VECTORS TO ANTITUMOR RUTHENIUM COMPLEXES

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In the past decade, silica nanoparticles have attracted considerable attention for their potential biomedical applications, owing to their biocompatibility, good water solubility and easy surface chemical functionalization. Given the soft conditions and control of the porous structure offered by some fabrication methods, these particles have been explored as effective drug delivery systems for a variety of therapeutic agents and diagnosis probes, in particular for those involved on the fight against cancer.

In this work, we report the fabrication of narrow dispersity organically modified hollow silica nanoparticles (nanocapsules) of ~60 nm of diameter and variable cavity size, synthesized at room temperature by combination of the sol-gel process and the water-in-oil emulsion technique, following different approaches. The nanocapsules were functionalized with a fluorinated silica precursor, in order to enhance their cellular uptake and to enable their use as contrast agent for ^{19}F NMR imaging.

The influence of some parameters related to the micellar system (water to surfactant ratio) and sol-gel reaction (nature and ratio of precursors and surface modifiers, pH, reaction time) on the morphology, chemical and porous structure of the nanoparticles were tested and assessed by complementary results obtained by transmission electron microscopy, diffuse reflectance infrared spectroscopy and nitrogen adsorption/desorption isotherms. Among those parameters, the pH of the mixture and the ratio of aminated surface modifiers, proved to account for the most significant changes.

The hollow particles were tested as nanocarriers for the azole-based antitumor ruthenium complex (H_2trz)[*trans*-$RuCl_4(N^2\text{-}Htrz)_2$], which belongs to the hottest family of non-platinium anticancer drugs. The complex was loaded into the nanocapsules during their synthesis stage, by dissolution in the aqueous phase of the micellar system. Different chemical structures of the drug were stabilized by adjustment of the aqueous phase pH, and their nature and interactions with the silica matrix were analysed by diffuse reflectance UV-Vis and infrared spectroscopies.

Keywords: *Nanoparticles; Sol-gel processes; Antitumor agents; Ruthenium;*

P-0717

APPLICATION OF A NTFET IMMUNOSENSOR TO THE DETECTION OF C-REACTIVE PROTEIN

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Due to their enhanced structural and electronic properties[1], the single-walled carbon nanotubes (SWCNT) have been used as the building blocks of biosensing/electronic devices. The fabrication of field effect transistors (FET) based on SWCNT (NTFET devices) represents a promising approach for applications on the electronic detection of biomolecules[2]. In this study, we report a NTFET device for the detection of C-reactive protein (CRP) by immunoreaction. Such acute-phase protein is considered as the current better validated inflammatory biomarker, being an indicator of the risk of cardiovascular diseases[3]. The antibodies specific for CRP (anti-CRP) were firstly immobilized by direct adsorption onto SWCNT. The analytical signal is calculated as the normalized drain current (I_D) after the exposure of various concentrations of CRP in relation to the I_D obtained after the immobilization of anti-CRP and SWCNT. The label-free biosensor is capable to detect various concentrations of CRP, which include the normal levels of CRP in serum, it requires small volume of sample, and it is portable with fast and simple analysis of CRP. In this work, we also present the microfabrication steps to the definition of FET devices which are in the origin of the applied biosensors to CRP.

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Keywords: *nanotubes; biosensors; immunochemistry;*

P-0718

DEPOSITION OF SILICON NANOSTRUCTURES BY AFM-LITHOGRAPHY

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The recent development of semiconductor devices and the ongoing miniaturization in all process steps led to an increasing demand for techniques to fabricate nanostructures. Among these techniques atomic force microscopy offers a precise control of nanostructure formation.[1-3] Furthermore, it has been shown that AFM-lithography offers a possible technique to produce electronic devices on the micro and nanometer scale.[2] AFM also provides a tool to operate and control chemical reactions in a defined area and to analyze the results simultaneously.[3, 4] Selected examples are electrochemical reactions[3] which make use of a bias voltage or thermally induced reactions which make use of a heated tip.[5, 6] Noteworthy, the reactions take place in a small area around the tip. This provides the possibility to carry out novel reactions and processes and to develop novel applications. A recent example is the decomposition of commercially available liquid diphenylgermane and diphenylsilane using AFM to provide germanium and silicon nanostructures with potential for microelectronic applications.[7] Herein we report our results on the use of diverse silanes of the type R_2SiH_2 and $RSiH_3$ for the deposition of silicon nanostructures using AFM-lithography from solution under atmospheric pressure.

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Keywords: *silicon; silanes; lithography; deposition; nanostructures;*

P-0719

SPRAY-ILGAR® DEPOSITION OF CONTROLLABLE ZNS NANODOTS AND APPLICATION FOR HIGHLY EFFICIENT THIN FILM SOLAR CELLS

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The spray ion layer gas reaction (Spray-ILGAR) technique produces homogeneous, compact metal chalcogenide films used as buffer layers for thin film solar cells with high efficiencies. It was a great challenge to elaborate this method for the deposition of nanodots. Now we show that high quality ZnS nanodots can be synthesized at low temperature by this sequential, cyclic and low cost method, which can be scaled up for industrial in-line production.

The choice of the process parameters allows the control of particle density and size. The unique sequential process results in the formation of the nanodot film with good properties. The dots are rather homogeneous in size, shape and composition, and tend to keep maximum distance from each other. In contrast, ZnS nanodots deposited by a continuous spray chemical vapor deposition (Spray-CVD) are larger and irregular in shape with inclusions of ZnO. By interpretation of the SEM, TEM, XPS and mass spectrometry results, the decomposition mechanism of Zn precursor and the self-limiting growth of ZnS nanodots are studied.

In addition, a passivation layer/point contact buffer composed of the ZnS nanodots covered by a homogenous In_2S_3 layer is produced consecutively by the Spray-ILGAR process. The ZnS reduces the recombination of the charge carriers at the absorber/buffer heterointerface which is one important position for performance loss in the chalcopyrite cells. The In_2S_3 in-between and on top of the ZnS dots is necessary for the charge carrier transport as ZnS has poor conductivity. The optimal ZnS dot density, In_2S_3thickness and process temperature with respect to optimum solar cell performance are investigated. Moreover, different In precursor solutions and different ZnS nanodot deposition methods are studied and compared. As compared to a pure In_2S_3 buffered cell, the solar cell efficiency with nano-ZnS/In_2S_3 buffer layer could be improved by about 1% absolutely upto 15.7%.

Keywords: *ZnS nanodots; Spray-ILGAR; buffer layer; thin film solar cells; passivation;*

P-0720

SELF-ASSEMBLED TETRAGONAL PRISMATIC NANOCAGE CAPABLE OF SELECTIVELY INTERACT WITH PI-ANIONIC SUBSTRATES

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The development of functional nanosized molecules has gained relevance thanks to the straightforward nature of the metal-directed supramolecular synthetic approach. In previous work we reported the use of macrocyclic dicopper(II) complexes as metal-organic molecular clips capable of self-assembling at room temperature with different di- tri- and tetracarboxylate linkers to yield nanomolecular 2D rectangles, and polyfunctional 3D trigonal prisms.[1, 2, 3] Among the various systems developed so far, discrete nanosized cage-like molecules are of particular interest for the implementation of specific functions because they provide an inner cavity that can be filled with functional guest molecules when brought together in solution.[4]

In this work we report the preparation of a new nanocapsule with A_4B_2 tetragonal prismatic geometry (where A corresponds to dipalladium macrocyclic complexes, and B corresponds to the tetraanionic form of palladium 5,10,15,20-tetrakis(4--carboxyphenyl)-porphyrin). The large inner void space of the obtained structure and the supramolecular affinity for guest molecules towards porphyrin-based hosts converts this nanomolecular 3D structure in a good candidate for host-guest chemistry. The interaction between the nanocage and different guest molecules has been studied by means of NMR, UV-vis, ESI-MS and DOSY experiments. Selective molecular recognition has been found for anionic, planar-shaped p-guests, in contrast to the absence of interaction for neutral aromatic or cationic substrates. Moreover using macrocycles of different lengths, we are able to tune the cage dimensions to accommodate guests of different sizes.[5]

The simplicity in the synthesis developed for the obtention of these complex architectures represents a step forward for the development of polyfunctional supramolecular nanovessels, with multiple applications.

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Keywords: *supramolecular chemistry; Nanostructures; Receptors; Anions; Palladium;*

P-0721

NEW LUMINESCENT HYBRID MESOPOROUS COPPER-SILICA MATERIALS

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Luminescent mesoporous organosilicas (PMOs) are usually prepared by total or partial co-condensation of organic chromophores bearing alkoxysilyl groups [1]. This method has several advantages like good pore volume values or absence of leaching, but the materials lacks of the tunability that coordination complexes possesses. Recently, we have reported the incorporation of various Pd(II) complexes bearing ligands with triethoxysilyl terminal groups into the framework of mesoporous silica and organosilica materials, using a facile solvent-free one-pot method [2]. In order to extend this synthetic method to the obtention of luminescent siliceous materials, and taking into account the growing interest that luminescent polynuclear d^{10} metal complexes are attracting [3] we firstly synthesize a new tetrametallic alkynyl copper(I) chromophore for its further co-condensation with tetraethoxysylane (TEOS), in the presence of a neutral surfactant. The new mesoporous hybrid luminescent metal complex-silica materials present a remarkable hydrothermal stability, considerably higher than those synthesized by the traditional post-synthetic routes, showing emissive properties that have been easily achieved by co-condensation of a strong emitter tetra-nuclear alkynyl copper cluster with TEOS; thus, opening the possibility of the synthesis of new materials with a great applicability potential [4].

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Keywords: *mesoporous materials; luminiscent; copper; chromophore; hydrothermal stability;*

P-0722

NANOCOMPOSITES BASED ON PHYLLOSILICATE AND METALLOSUPRAMOLECULAR POLYELECTROLYTES: MODULAR COMPOUNDS FOR ELECTRORHEOLOGICAL FLUIDS

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Particles dispersed in a non-conductive oil can respond to an electric field. If the particles get polarized they form column like structures, which affect the viscosity. Those dispersions are called electrorheological fluids (ERF). For such an ERF we prepared a new nanocomposite based on the phyllosilicate clay Montmorillonite (MMT) and metallo-supramolecular polyelectrolytes (MEPE). To examine the electrorheological properties, we tested the rheological response of different nanocomposite/silicone oil dispersions to an electric field. The examined samples show a distinctive ER effect with only small active substance necessary. Furthermore the observed currents are very small, which is essential for a potential application.

Metallo-supramolecular polyelectrolyts based on a ditopic bisterpyridine ligand and different metal ions are intercalated into MMT. The intercalation is verified by powder X-ray diffraction, thermal analysis and IR spectroscopy. The powder diffraction pattern shows a shifted (001) reflection indicating a widening of the interlayer spacing and the differential thermal analysis display an increased decomposition temperature. These results indicate an inclusion of the MEPE rods into the interlayer of MMT. IR spectroscopy confirms the intercalation.

The storage and the loss moduli of the dispersed nanocomposites are measured with an oscillating rheometer as a function of the potential within a range from 0 to 2 kV/mm. The nanocomposite shows an electrorheological (ER) effect depending on concentration (2, 3, 5 and 10 wt %). With a content of 10 wt % the storage modulus G' of a nanocomposite dispersion increases from 20 to 2700 Pa. We were able to examine the structure of the polarized particles under the microscope and an applied electric field. The effect is accompanied by small currents (0.01 mA/mm²). Pure MMT shows under the tested conditions only a small ER-effect, indicating the contribution of the MEPE to the effect.

Keywords: *Supramolecular chemistry; Clay; Electrorheological Fluid; Intercalations;*

P-0723

FABRICATION AND CHARACTERIZATION OF NANOMETRIC OXIDE COATINGS WITH TUNABLE STIFFNESS

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The design of surfaces with controlled stiffness is attractive for applications ranging from controlling biological cell growth to mechanical and electrical engineering design. We report the creation of layered composites with tunable surface stiffness achieved by coating a soft PDMS polymer (~10 microns) with a stiff film of amorphous titania (2 - 50 nm). The oxide layer is smooth (6 nm rms roughness at 2 μm^2 image size), and crack-free. Air plasma pre-treatment of the PDMS was used to promote adhesion of the titania overlayer.

Nanomechanical characterization of the layered structure has been done by a number of different experimental approaches and the results have been modeled. The surface mechanical properties of the samples have been probed using both instrumented nanoindentation and atomic force microscopy-based nanomechanical characterization. The results have been compared to finite element analysis (FEA) simulations.

By fitting the FEA simulations with the experimental AFM curves it is shown that the hard titania film and the soft PDMS substrate individually maintain their characteristic elastic moduli, while the stiffness of the vertical nanocomposite can be controllably modified by changing the thickness of the stiff layer. Liquid phase deposition of the oxide allows control of its thickness at the nm level.

This synthetic approach can be quite versatile, and can, in principle, be extended to different oxides and a wide range of thicknesses. It allows variation in mechanical properties of the surface while maintaining a constant surface chemistry. This exploratory work is a first step towards defining the range of surface stiffnesses that can be achieved in this way, as well as developing general methodologies for their characterization.

P-0724

FUNCTIONAL SYNTHETIC VESICLES: BIOMIMETIC SENSING & CATALYSIS

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Cell membranes play a key role for the function of living organisms. Thus the development of artificial membranes is of great interest – not only as biological mimics but also to open up ways to new functional materials.

We have developed synthetic vesicles based on natural phospholipids which were doped with artificial functional amphiphiles. Amongst these membrane-embedded compounds are artificial receptors for biomolecule recognition,[1] fluorescent dyes for optical sensing[2] and transition metal catalysts for catalytic transformations at the membrane-water interface.[3] This way we have established a novel approach towards modular luminescent chemosensors and highly-active supramolecular catalysts.

Characterization of our soft nanoparticles includes methods like DLS, AFM, Cryo-TEM, DSC, SPR, ITC and optical spectroscopy. The embedded functional amphiphiles are assumed to form domains within the phospholipid membranes and under certain conditions respond to external stimuli by spatial rearrangements. Currently we pursue the development of multi-receptor surfaces which respond to specific analytes by defined emission patterns like FRET-signatures and photopolymerized particles as molecularly imprinted materials.

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Keywords: *Vesicles; Sensors; Fluorescence; Self-assembly; Heterogeneous catalysis;*

P-0725

PHOTOACTIVE ION EXCHANGE POLYSTYRENE NANOFIBER TEXTILES

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The nanofiber textiles prepared by electrospinning with an encapsulated photosensitizer efficiently photogenerate singlet oxygen, which is able to oxidize external chemical and biological substrates/targets [1–3]. Herein we present sulfonated elektrospun polystyrene (PS) nanofiber textiles with externally bound cationic photosensitizers and/or encapsulated nonpolar *meso*-tetraphenylporphyrin or aluminum phthalocyanine chloride. We used two diferent types of cationic photosensitizers, namely 5,10,15,20-tetrakis(1-methyl-4-pyridinio)porphyrin tetra(p--toluenesulfonate) and methylene blue. The materials were studied by microscopic methods, steady state and time-resolved absorption and fluorescence spectroscopy. All nanofiber materials exhibited photogeneration of singlet oxygen and singlet oxygen mediated delayed fluorescence (SODF). Prompt and SODF was used as a sensitive tool for estimation of an optimal amount of externally bond photosensitizer for maximum generation of singlet oxygen. Doped sulfonated PS nanofibers exhibit the oxidation of an external substrate and antibacterial activity against *E. coli*. when activated by visible light. Ever moderate sulfonation strongly increase the wettability of hydrophobic PS nanofibers yielding to increase of antibacterial activity of nanofibers with an encapsulated photosensitizer. Extensive sulfonation of nanofibers is associated with postpolymerization crosslinking effect increasing the resistence of nanofiber material to nonpolar media but decrease oxygen diffusion in polymer.

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Keywords: *Photochemistry; Photophysics; Singlet oxygen; Porphyrinoids; Phthalocyanines;*

P-0726

PHOTO-ACTIVE SPIROPYRAN-BASED INTERLOCKED SYSTEMS

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Interlocked molecules, such as catenanes and rotaxanes, are considered models of artificial molecular machines since they can transform an energy input (chemical, electrochemical or optical) into a mechanical motion of their components without dissociation.[1]

An important precursor for the synthesis of rotaxanes and catenanes are pseudorotaxanes. In a previous work we have shown that 1,2-bis(pyridinium)ethane axles and macrocyclic ethers, like dibenzo-24-crown-8 ether **[DB24C8]** and disulfonated-dibenzo-24-crown-8 ether **[DSDB24C8]**$^{2-}$, are capable of assembling into [2]pseudorotaxanes, which then can be transformed into [2]rotaxane type complexes.[2]

Now, we have developed a new [2]pseudorotaxane motif by substitution of one pyridinium unit on the axle by a spyropiran moiety (SP), which can be isomerized into a monocationic merocyanine fragment (ME) by an optical or chemical stimulus.[3] Isomerization of SP into ME changes the crown ether affinity towards the axle. Here, we will discuss the behaviour of the axle in presence of **[DB24C8]** or **[DSDB24C8]**$^{2-}$, in several different solvents. Also, we will present our progress on the development of [2]rotaxane systems where the motion can be controlled by reversible structural changes on the axle.

In summary, we have designed a new spiropyran-based interlocked molecule where the photo-isomerisation of the SP fragment triggers the motion of the components.

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Keywords: *Supramolecular chemistry; Rotaxanes; Photochromism;*

P-0727

INTRAMOLECULAR FLUORESCENCE QUENCHING IN 2,6-SULFANYL-CORE-SUBSTITUTED NAPTHALENEDIIMIDE

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Herein we report the successful synthesis of a tailor-made 2,6-sulfanyl-core-substituted naphthalenediimide (NDI) with an efficient intramolecular fluorescence quenching.

Core-substituted NDIs have tunable photoluminescent properties based upon the substitution pattern at their core and are easily functionalizable organic *n*-semiconductors, which belong to the class of fluorophores. By varying the core substitution of a particular NDI very low or high fluorescence quantum yields can be obtained. According to literature those yields are not only depending on the core substitution, but also on conformational changes and the involved electron transfer processes.

Recently, Pugliesi et al.[1] published the first time-resolved study on the charge transfer rate from a core substituent to the NDI unit. In particular, they compared different model compounds with three different moieties (alkyl, benzyl and phenyl), which were directly attached to a 2,6-sulfanyl-core-substituted NDI, by investigation of their fluorescence quenching behavior. Only if an electron donor such as a phenyl unit was linked in plane with the core substituent an ultrafast and efficient fluorescence quenching was detected.

Inspired by these results a tailor-made model compound has been designed and synthesized which consists of a symmetrical 2,6-sulfanyl-core substitution. Reliable synthetic procedures have been subsequently developed to isolate the desired target structure only after 6 linear steps. The phenylsulfanyl substituents are fixed in such way that the fluorescence quenching could be drastically increased. This has been proven by measuring the absorption and fluorescence spectra of the model compound.

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Keywords: *Fluorescence; Fluorescence spectroscopy; Nanostructures; Napthalenediimide; Ab initio calculations;*

P-0728

INVESTIGATION OF PD AND PDO BASED CATALYSTS IN THE OXIDATION OF PRIMARY AND SECONDARY ALCOHOLS

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Oxidation of primary and secondary alcohols plays a fundamental role to produce carbonyl compounds as building blocks in organic synthesis, for example in the fragrance and pharmaceutical industries[1]. In our work we focus on the usage of palladium based catalysts in alcohol oxidation. It is still under debate whether Pd^0 or PdO, is the active site for oxidation processes[2]. Our investigations show, that Pd/TiO_2 and PdO/TiO_2 show similar activity in the gaseous phase oxidation of 2-propanol. In order to understand this finding we used comparative experiments to investigate the formation of the active material. The samples were prepared by colloidal deposition on titania[3] using $PdCl_2$ as precursor. Information about the catalyst material was obtained from PXRD, TEM and XPS.

Detailed investigation on the temperature dependents (RT-160°C) in methanol oxidation over Pd/TiO_2 and PdO/TiO_2 (followed by on-line QMS) show, that PdO is inactive below 100 °C, while Pd/TiO_2 is already active at room temperature. Multiple cycle experiments show that PdO gets activated in the presence of gaseous alcohols, reaching high conversion in methanol oxidation, comparable to Pd/TiO_2 suggesting the formation of metallic palladium as active species in alcohol oxidation. To prove this change of PdO to Pd, near ambient pressure XPS is performed at different temperatures.

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Keywords: *Palladium; Nanoparticles; Gas-phase reactions; Oxidation; Alcohols;*

P-0729

GERMANIUM NANOPARTICLE FORMATION FROM DIFFERENTLY SUBSTITUTED MOLECULAR PRECURSORS
– WHAT IS THE ROLE OF HYDRIDE?

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One route to germanium nanoparticle formation utilizes high temperature decomposition of organogermanium precursors. We have previously investigated the influence of organic substitution on germanium-rich oxide formation for solid-state synthesis of germanium nanocrystals, and found that the elimination mechanism of the organic group plays an important role in the formation temperature.[1] In this talk, we will present the findings from investigating different substitution patterns of the molecular precursor n-butylgermane.

Tetra-n-butylgermane has been found to decompose at 285 °C to give elemental germanium and various organic byproducts. We will discuss the impact that hydride-substitution has on this decomposition process and the subsequent formation of germanium nanoparticles as we progress from tetra- to tri-, di- and mono-n-butyl-substitution.

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Keywords: *Germanium; Nanoparticles;*

P-0730

MESOPOROUS GALLIUM OXIDE THIN FILMS AND THE CONVERSION OF THE WALL MATERIAL INTO NON-OXIDES BY SUPERCRITICAL FLUID TREATMENT

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We develop the synthesis method of mesoporous gallium oxide (Ga_2O_3) thin films by using a non ionic surfactant (F-127) as a structure directing agent. None of the previously reported the mesoporous Ga_2O_3 has a thin film structure. The mesorporous Ga_2O_3thin films are expected to utilize as acid-catalysts or other functional materials. Furthermore the mesoporous Ga_2O_3 thin films can be converted to Ga_2S_3 films, which are semiconductor materials, by supercritical fluid reaction. All films have wormlike structure and about 10nm pore sizes. Also we can control the film thickness in the range of 40–340nm depending on the composition of gallium source (GaN_3O_9) and F127 of the coating solution. The mesostructure of the films was characterized by transmission electron microscopy (TEM) and scanning electron microscopy (SEM). The elemental composition was determined by energy dispersive spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS).

Keywords: *Gallium oxide; Mesoporous; Supercritical fluid; Gallium sulfide;*

P-0731

TRANSVERSE RELAXIVITY INVESTIGATIONS OF MAGNETIC MESOPOROUS SILICA NANOPARTICLES

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Mesoporous silica nanoparticles (MS NPs) have attracted much interest in recent years due to their potential as effective nanotherapeutic devices. Their large pore volume provides excellent drug delivery abilities, and well-understood silica chemistry presents many opportunities for the incorporation of multiple functionalities. Especially important for both clinical trials and subsequent personalized patient care is the incorporation of contrast agents such as Fe_3O_4 nanoparticles for T_2 magnetic resonance imaging (MRI). These magnetic core/shell nanoparticles have been developed by several research groups, but none have investigated the effect of synthetic conditions on magnetic relaxivity (r_2), the indicator of contrast agent quality. In addition, while many of the literature MS NP systems have provided *in vivo* contrast post-injection, personalized medicine will require high-quality imaging hours or days after administration. To this end, MS NPs with imaging capabilities must retain particle stability in biological environments, and the effectiveness of the contrast agent must be maintained. To our knowledge, no long term studies on magnetic MS NP image contrast have been previously reported. Studies on parameters affecting r_2, both on short and long time scales, are called for. In this work, we probe the effects of silica shell thickness, iron oxide core synthesis, and hydrothermal treatment on the r_2 of magnetic MS NPs. In addition, we examine short- and long-term stability of r_2 in water, phosphate buffered saline, and acidic media to mimic biological environments. We show that a simple hydrothermal treatment proves particularly effective in maintaining colloidal and r_2 stability and in providing resistance against acid degradation in biological environments.

Keywords: *Mesoporous Materials; Magnetic Properties; Nanoparticles; Imaging Agents; Drug Delivery;*

P-0732

NITROGEN-DOPED GRAPHENE CREATED WITH DIFFERENT PRECURSORS

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Nitrogen-doped graphene is of general interest for electronic devices. We try to include nitrogen into the graphene lattice by CVD methods and successfully fabricated high quality nitrogen-doped graphene from CVD method of simple molecular precursors like pyridine.

The graphene quality is related to the molecular precursor and the decomposition parameters. For example, the temperature dependence was studied in detail in the range from 600–1000 °C. As the temperature increased, the graphene formation was improved and well-separated D, G and 2D peaks were generated. It is considered that the decomposition and the following graphene growth are promoted at higher temperatures. The optical and morphological properties of nitrogen-doped CVD graphene were characterized and compared for understanding the graphene formation.

Keywords: *Chemical vapor deposition; Nitrogen-doped graphene; Raman spectroscopy;*

P-0733

SUPRAMOLECULAR HELICAL NANOFIBER FORMATION FROM THE SELF-ASSEMBLY OF CYTIDYLIC ACID-APPENDED BOLAAMPHIPHILE WITH DI- AND TRI-CARBOXYLIC ACID

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Bottom-up approach, which refers to the build-up of materials from molecular components, has attracted much attention to many researchers in the field of nanotechnology. In particular, combination of self-assembly and molecular recognition, as often seen in biomolecules, is one of the elegant strategies to make well-defined nanostructures. We chose DNA as a motif because the excellent property of self-assembly with molecular recognition ability is already incorporated into DNA molecules.[1–2] In addition, the production of materials using renewable bioresources is now a challenging theme in the field of bottom-up nanotechnology. Herein, the binary self-assembly of 1, 18-cytidylic acid-appended bolaamphiphile (C18C)[3] in which a 3'-phospholylated cytidine moiety is connected to both ends of an octadecamethylene chain, and di- or tricarboxylic acids is reported. Atomic force microscopy (AFM), circular dichroism (CD), UV absorption, and Fourier-transform infrared (FT-IR) spectroscopy, and electrospray ionization-Fourier-transform ion cyclotron resonance (ESI-FTICR) mass spectrometry experiments revealed the binary self-assembly of C18C and malonic, succinic, glutaric, or citric acids formed nanofibers through molecular recognition. Moreover, left-handed helicity was observed in the nanofiber obtained from the binary self-assembly of C18C and citric acid (CA) with diameters, lengths, and pitches ca. 6 – 7 nm, several hundred nm to 5 μm, and ca. 30 – 40 nm, respectively. Based on the observations, we performed the self-assembly of C18C in lemon juice containing citric acids, and succeeded in the formation of the left-handed helical nanofiber by the fusion of supramolecular chemistry and renewable biomaterials.[4]

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Keywords: *Self-assembly; Nanofibers; Supramolecular Chemistry; Bolaamphiphiles; Nucleotides;*

P-0734

ALIGNED GROWTH OF GOLD NANORODS IN PMMA CHANNELS: PARALLEL PREPARATION OF NANOGAPS

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The fabrication of electrode pairs separated by a few nanometers is a fundamental challenge in nanotechnology.[1, 2] Nanogaps between metallic electrodes or nanoparticles are applied within diverse areas such as single-molecule electronics, plasmonics and spectroscopy. In single-molecule electronics the goal is to utilize single molecules as electrical components by understanding how electron transport through molecules is governed by the chemical structure of a molecule in order to be able to tailor its specific function. Here, we demonstrate alignment and positional control of gold nanorods grown in situ on substrates using a seed-mediated synthetic approach. Alignment control is obtained by directing the growth of spherical nanoparticle seeds into nanorods in well-defined poly(methyl methacrylate) nanochannels. Substrates with prepatterned metallic electrodes provide an additional handle for the position of the gold nanorods and yield nanometer-sized gaps between the electrode and nanorod. The nanogaps are electrically characterized, and to test the stability of the nanogaps, electronically active oligo(phenylenevinylene) (OPV) molecules are inserted into a nanogap junction by solution deposition, which results in an increase in the electrical conductance of several orders of magnitude compared to the empty nanogap.

The presented approach is a novel demonstration of bottom-up device fabrication of multiple nanogap junctions on a single chip mediated via in situ growth of gold nanorods acting as nanoelectrodes.[3]

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Keywords: *Nanoparticles; Nanostructures; Molecular electronics;*

P-0735

SILICA CAPSULE WITH ADJUSTABLE SHELL MORPHOLOGY

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Hollow spheres or capsules are some of the most actively investigated structures due to their potential applications in areas including biology, synthesis, photonics and catalysis. Various practical applications often require robustness and flexibility in microcapsule-based materials. Structure-adjustable capsules have been fabricated from inorganic components by using a self-template method. The resulted microcapsules possess flake shell which is composed by silica sheet with several nanomenter thickness. The capsules shrink under thermal stimulus and their structures can be adjusted by treatment at different pH. The flake shell capsules were shown high loading efficiency on drug molecules and DNA. In addition, the structrual flexibility in tuning of shell pore diameters leads to tailored drug release over prolonged periods.

P-0736

EFFICIENT ULLMANN CROSS-COUPLINGS USING PD NANOPARTICLES

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The Ullmann cross-coupling of aryl halides is an old but very important rout for synthesis of dissymmetric biaryls specially since introducing the palladium compounds as catalyst.[1] In the other hand, palladium nanoparticles have unique applications as catalyst in a wide variety of reactions.[2] Therefore, in continuation of our previous study on cross-coupling reactions[3–4], we synthesized Pd nanoparticles via a simple method using polyethyleneglycol as both reducing agent and stabilizer. The efficiency of these palladium nanoparticles was investigated in the cross coupling reaction of aryl halides. A wide variety of substrates bearing different functional groups (electron withdrawing and electron donating groups) in para position were sufficiently coupled to yield the desired functionalized biaryls.

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Keywords: *Cross-Couplings; Nanoparticles; Palladium;*

P-0737

FABRICATION AND CHARACTERIZATION OF ZNFE$_2$O$_4$@TIO$_2$ SUBMICRON PARTICLES FOR MAGNETIC PHOTOCATALYST

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In recent years, superparamagnetic submicron materials have become particularly crucial in research area for biomedical application such as drug delivery, biosensor, and photocatalyst. In order for magnetic submicron materials to be applied in this kind of application, it needs to be soluble in water solution and has to have high saturated magnetization in mild magnetic field at room temperature. Among the reported photocatalysts, titanium dioxide(TiO_2) is one of the most studied semiconductors for photocatalytic reactions because of its high activity, chemical stability, robustness against photocorrosion, low toxicity and availability at low cost, especially for the detoxification of water and air. However, practical applications of photocatalysis are limited because of several problems arising from using fine TiO_2 powders in photochemical process such as separating and recycling of the photocatalyst. In order to avoid these technical problems, several approaches have been taken. For example, powder type photo-catalysts have been immobilized on various supports, including glasses, silica, polymers, and film type photocatalysts have been prepared through sol-gel, CVD, oxidation of Ti plate etc. In this study, we synthesized monodispersed superparamgnetic $ZnFe_2O_4$ submicron particles by using a one-step solvothermal method. To induce the photocatalytic function, we coated TiO_2 on $ZnFe_2O_4$ nanoparticles by atomic layer deposition(ALD). The submicron particles of $ZnFe_2O_4$ and $ZnFe_2O_4@TiO_2$ was analyzed by using X-ray diffraction(XRD), field emission scanning electron microscopy(FE-SEM), and transmission electron microscopy(TEM). The diameter of prepared $ZnFe_2O_4@TiO_2$ shows a monodispersed size distribution of 200±10 nm and 10nm in shell thickness. The magnetization was measured by a vibrating sample magnetometry(VSM). The magnetization curve of two samples have superparamagnetic behavior showing no hysteresis. The recyclable $ZnFe_2O_4@TiO_2$ demonstrated an excellent catalytic ability to degrade 2,4,6-tricholorophenol(2,4,6-TCP) in aqueous solution.

Keywords: *photochemistry; magnetism; nanoparticles; nanostructures; Spinel phases;*

P-0738

PREPARATION AND CATALYTIC ACTIVITY OF NANOAG@MONTMORILLONITE COMPOSITE MATERIALS

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In recent years, silver nanoparticles (Ag NPs) have belonged to intensively studied nanomaterials particularly due to their unique electrical, optical, catalytic or biologic properties. The increase of application potential of Ag NPs can bring their anchoring on a solid substrate. As a suitable materials for anchoring of Ag NPs clay minerals can be used especially due to their large surface area and good economic accessibility [1].

This work is aimed on the preparation and catalytic activity of composite materials containing silver nanoparticles (Ag NPs) anchored onto solid surfaces of the two types of clay minerals – calcium and sodium form of montmorillonite. The aqueous dispersion of silver NPs was prepared by reduction of $[Ag(NH_3)_2]^+$ complex cation by maltose disaccharide [2]. The average size of the prepared particles was about 30 nm with narrow size distribution. Nanocomposite materials were prepared using simple adsorption of the silver NPs from their aqueous dispersion on the afore mentioned types of clay minerals.

Catalytic activities of nanoAg@CaMMT and nanoAg@NaMMT composite materials were studied on a model reduction reaction of 4-nitrophenol to 4-aminophenol by sodium borohydride in aqueous solution. The rate constant of the reaction was obtained from the spectral changes of absorption peak of 4-nitrophenolate ions at 400 nm with time.

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Keywords: *Adsorption; Nanoparticles; Silver;*

P-0739

INTERMETALLIC CU-ZN NANOPARTICLES IN STRUCTURE OF IR-PYROLYZED POLYACRYLINITRILE

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Metal-carbon nanomaterials are of great interest for researchers due to wide spectrum of their practical application. The investigation of phase content, structure and morphology of metal-carbon nanocomposites as a function of preparation conditions opens up possibilities for regulation of their properties.

The goal of research work is development of preparation method of metal-carbon nanocomposites based on IR-pyrolized polyacrylonitrile (IR-PAN) and bimetallic Cu-Zn nanoparticles and investigation of their structural characteristics.

Metal-carbon composites were firstly prepared under the conditions of IR-pyrolysis of a precursor based on common solution of PAN, copper and zinc acetates in dimethylformamide. Pyrolysis was performed in an IR-chamber of a setup for pulse photon annealing. The carbonization of PAN and metals reduction in the presence of hydrogen which is released during dehydrogenation of backbone polymer chain of PAN took place simultaneously. In the obtained nanocomposites nanoparticles of intermetallic compounds are finely dispersed in graphite-like structure of IR-PAN.

According to the X-ray difraction data for nanocomposites prepared at 300–500 °C there was one intensive peak corresponding to $CuZn_5$ intermetallic compound reflection angles. At 500<T<<t<700°C intermetallide of another content begins separate out. At T>700 °C two peaks in the area of 54,5 and 55,5 ° corresponding to $CuZn_5$ and $CuZn_2$ are identified. In this case the share of $CuZn_2$ nanoparticles rises with the IR-irradiation intensity increase.

Interplanar distances (101) for bimetallic nanoparticles were determined: d=0,2107 nm and 0,2075 nm for $CuZn_2$ and $CuZn_5$ respectively.

TEM investigation showed that intermetallic nanoparticles $CuZn_5$ and $CuZn_2$ are finely and homogeneously distributed in graphite-like structure of IR-PAN. They have spherical form with sizes within the limits 7<d<17 nm.

Thus nanocoposites with intermetallic Cu-Zn nanoparticles finely dispersed in graphite-like structure of IR-pyrolized PAN were obtained firstly. Prepared nanomaterials may be applied as heterogeneous catalysts for important industrial processes such as methanol stem reforming.</t<

Keywords: *copper; zinc; nanoparticles; X-ray difraction;*

P-0740

CONSTRUCTION OF HIGH-PERFORMANCE ARTIFICIAL MEMBRANE FUSION SYSTEM WITH TARGET-SELECTIVITY

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Thewell-programmed and controlled membrane fusion phenomenon is one of thefundamental events in the life of eukaryotic cells and these fusion reactionsare mediated by many kinds of membrane fusion proteins to overcome largeenergetic barriers in biological membranes. Membrane fusion proteins havetarget recognition and fusion accelerative domains, where some synergisticallyworking elements are essential for target-selective and highly effective nativemembrane fusion systems. In this work, novel membrane fusion devices bearingsuch domains were designed and constructed. Furthermore, we report herein characterizationof liposomal membrane fusion reactions by the use of the designed devices. Weselected a phenylboronic acid derivative as a recognition domain for asugar-like target and a transmembrane-peptide (Leu-Ala sequence) domaininteracting with the target membrane and accelerating the fusion process.Artificial membrane fusion behavior between the synthetic devices in whichpilot and target liposomes were incorporated was characterized by lipid-mixingand inner-leaflet lipid-mixing assays. In consequence, the devices bearing bothof the recognition and transmembrane domains brought about a remarkableincrease in the initial rate for the membrane fusion compared with the devicescontaining the recognition domain alone. In addition, a weakly acidicpH-responsive device was also constructed by replacing three Leu residues inthe transmembrane-peptide domain by Glu residues. The presence of Glu residuesmade the acidic pH-dependent hydrophobic alpha-helix formation possible asexpected. The target-selective liposome-liposome fusion was accelerated in aweakly acidic pH range when the Glu-substituted device was incorporated inpilot liposomes. The using of this pH-responsive device seems to be apotentially strategy for novel applications in a liposome-based deliverysystem.

Keywords: *liposome; membrane fusion; phenylboronic acid derivative; target recognition; transmembrane-peptide;*

P-0741

FUNCTIONALIZED MULTIWALLED CARBON NANOTUBES FOR THE DELIVERY OF THERAPEUTIC ANTISENSE OLIGODEOXYNUCLEOTIDES AGAINST NON-MUSCLE-INVASIVE BLADDER CANCER

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Antisense oligodeoxynucleotides (AS-ODNs) are able to specifically down-regulate the expression of tumor-related genes like VEGF and survivin. Hence, they have a great potential as anticancer agent. In case of non-muscle-invasive bladder cancer the biggest challenge is an effective delivery of AS-ODNs and other drugs to the bladder wall before they can be excreted.

Multiwalled carbon nanotubes (MWCNTs) are known to easily enter cells. Additionally, the surface of MWCNTs can be functionalized for different purposes like drug delivery and for increased mucoadhesive properties. In this way, they can enhance the local drug concentration at the mucous membrane of the bladder wall. For the delivery of AS-ODNs a DNA anchoring strand was coupled to MWCNTs and the complementary AS-ODNs can hybridize with these DNA-MWCNTs. Since hybridization of complementary DNA strands is a reversible process the AS-ODNs can be easily released from the carrier after the delivery to the bladder wall. Furthermore, the releasing behaviour of AS-ODNs can be controlled by adjusting the hybrid stability. For this reason, functionalized MWCNTs have a great potential as carriers for AS-ODNs.

MWCNTs were produced by chemical vapour deposition. By washing the MWCNTs with nitric acid they were simultaneously oxidized. Afterwards, they were functionalized by a 1,3-dipolar cycloaddition reaction to insert hydroxyl groups for an improved stability of dispersion in aqueous solutions. DNA was coupled to these functionalized MWCNTs by covalent binding or helical wrapping. Afterwards AS-ODNs could hybridize with DNA-MWCNTs. Since the AS-ODNs were fluorescence-labelled subsequent desorption was investigated by fluorescence spectroscopy at different buffers and temperatures as well as under physiological conditions in urine and as function of varied anchoring strand sequences.

The delivery of AS-ODNs by MWCNTs demonstrates a novel strategy to improve the therapy for non-muscle-invasive bladder cancer. In this way, the high recurrence and progression rates should be decreased.

Keywords: *Nanotechnology; Nanotubes; Oligonucleotides; Drug delivery; Cancer;*

P-0742

MACROCYCLES AS ORGANOCATALYST – A NEW STRATEGY FOR ROTAXANE SYNTHESIS

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Mechanically interlocked supramolecules such as rotaxanes and catenanes are of current interest not only because of their molecular topology but also as basis for the development of artificial molecular machines. One well-known example for such host molecules and rotaxane wheels are tetralactam macrocycles (TLM). They provide four converging hydrogen bonds to interact with suitable axle molecules and therefore have been frequently applied in templated rotaxane synthesis. As we report herein, the TLM may not only function as a host molecule but may also activate guest molecules. Several reactions like Diels-Alder reactions, Michael additions, electrophilic bromination can thus be organocatalytically accelerated. Basic requirement is the choice of a suitable reactant that fits geometrically into the cavity of the wheel and thus is activated by hydrogen bonding to the four amide protons.

As rotaxane synthesis is often assisted by the template-directed preorganization of the individual building blocks “via” metal-coordination, hydrogen bonding or donor-acceptor interactions, we combined the old template strategy with the observed catalytic effect into a new one: In addition to the preorganization of axles with suitable binding motifs within the macrocycle the following rotaxane formation is accelerated by the host. Our results suggest the interplay of organocatalysis and templates to become a powerful synthetic strategy for functional molecules.

Keywords: *Rotaxane; Organocatalysis; Diels-Alder reaction; Michael addition;*

P-0743

HOST-GUEST COMPLEXES: HOW SMALL STRUCTURAL CHANGES AND MULTIVALENT EFFECTS CAN HAVE A LARGE IMPACT ON BINDING PROPERTIES

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The binding behavior of differently substituted diamide axle molecules to Hunter/Vögtle tetralactam macrocycles was studied with a combination of NMR titration, ITC experiments, crystal structures, and density functional calculations. Therefore, it could be shown that substituents have a decisive effect on the binding situation: guests with alkyl or alkenyl chains attached to the diamide carbonyl groups have a significantly higher binding affinity to the macrocycle than guests with benzoyl amides and their substituted analoga. In these cases, the electronic effects of para-substituents at the benzoyl moieties determine the binding affinities. Electron donating substituents increase, while electron-withdrawing substituents decrease the binding energies until nearly no binding could be observed anymore.

These results not only have an impact on the design of template effects for rotaxane synthesis, but all the more they are the basis for our synthesis of multivalent host-guest complexes based on pseudorotaxane structure, which are formed through an interplay of self-organization, self-sorting, template effects and multivalent interaction.

The synthetic accessibility of these components allows the design of analogous series of pseudorotaxanes with different number of binding sites and thus a systematic evaluation of multivalent binding situations can be realized.

Keywords: *Pseudorotaxanes; Host-guest complexes; Multivalency; NMR titration;*

P-0744

SYNTHESIS AND SUBSEQUENT USE OF IRON OXIDE NANOPARTICLES AND SILVER NANOPARTICLES

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Nanoparticles of magnetic iron oxides, magnetite and maghemite, present materials, which are due to their specific properties used as biological sensors, catalysts, adsorbents, carriers of drugs, contrast agents in magnetic resonance and in many other applications. Nanoparticles of silver are regarded to be another interesting nanomaterial, they are commercially used because of their high antibacterial activity. By combining these nanoparticles, we gain nanocomposites of iron oxide nanoparticles and silver nanoparticles - $Ag@Fe_3O_4$ and γ-$Fe_2O_3@Ag$. Magnetic nanocomposites present one of the remarkable developed materials of nanotechnology research. Thanks to their magnetic properties, they can be efficiently transported to the required place of the human body by external magnetic field.

We prepared these nanocomposites by the chemical reduction of silver ions in the presence of magnetic iron oxides, polyacrylic acid sodium salt and D-maltose. The prepared nanocomposites were characterized by transmission electron microscopy, SQUID magnetometry, X-ray powder diffraction, atomic absorption spectroscopy and Mössbauer spectroscopy. Both nanocomposites were tested for their antibacterial activity and cytotoxicity. For tested bacteria species there was obtained minimal inhibition concentration (MIC) ranges from 15.6 mg/L to 125 mg/L and for tested candida species the MIC levels range from 1.9 mg/L to 31.3 mg/L. To the contrary, acute cytotoxicity against mice embryonal fibroblasts was observed at concentrations of higher than 292 mg/L for γ-$Fe_2O_3@Ag$ nanocomposite and 430 mg/L for nanocomposite $Ag@Fe_3O_4$.

Keywords: *nanoparticles; iron; silver; magnetic properties;*

P-0745

SOLVENT FREE PRINTING OF ELECTRONIC CIRCUITS WITH SILVER NANOPARTICLES PREPARED BY A GREEN AND CONTROLLED SYNTHESIS

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Progresses in the fabrication of printed electronics have opened the door for the production of portable, flexible and very low-cost electric circuits. Concrete examples for printable electronics are photovoltaics, antennas, flexible displays and batteries, sensors, RFID tags, lighting devices, resistive heaters and transistors. It is known from literature that recent investigations focused on the integration of conductive tracks on flexible polymer foils, paper and textile fabrics.[1, 2, 3]

For the fabrication of printed electronic devices different printing technologies can be used such as screen printing, gravure, offset lithography, flexography or inkjet printing. Inkjet printing offers a number of advantages compared to the other printing techniques. It is a digital printing technology and therefore no special templates have to be fabricated and it is a nonimpact printing procedure with inks of low viscosity.

Since the end oft the 20th century, special fabric printers using colour ink-jet technology by digital printing are inexpensively available on the market. Investigations were made to use these standard commercial printers for the fabrication of highly conductive patterns on textile fabrics. Therefore special water-based, non-toxic, solvent-free, ‘green‘ inks had to be prepared.

Silver was chosen as conductive material because it has the highest electrical conductivity of all metals. During the last years, the synthesis of silver nanoparticles has attracted tremendous interest. Different synthetic methods have been developed and in few cases details on mechanism of formation are known.[4, 5] Here, we present a new synthesis that allows for controlling the nanoparticle size and thus preparing water-based silver inks for textile printers. The particles were characterized using different techniques like DLS, UV/Vis spectroscopy and SEM micrographs. An overview of ink preparation will be given on the poster.

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Keywords: *Nanotechnology; Silver; Sustainable Chemistry;*

P-0746

TOPOCHEMICAL REACTIONS IN FULLERENE BASED CRYSTALS

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Topochemical reactions in fullerene-based crystals can be originated from crystal- and molecular structural features. Fullerenes are the 3D analogues of planar aromatic systems, their reactivity comes from reactive double bonds. The basic material, C_{60} has various solid phase reactions in pure crystals and in cocrystals too.

In pure fullerene crystals photopolymerization can occur by the effect of light resulting small sized cycloadduct fullerene homo-oligomers. We worked out a new method to produce C_{60} photopolymer in gram scale[1], and we detected several small sized oligomers, and obtained solvent-free photo-dimer crystals.

Based on the relatively big size of the fullerenes big cavities can be found in the crystal structure with different symmetries. Small guest molecules can be built into these voids. We showed that with reactive guest molecules, like piperylene or small azides topochemical reactions can be carried out with high selectivity and good yield.

Several high symmetry cocrystals arise with the combination of fullerenes and cubanes[2]. These supramolecular crystals have unusual dynamics based on the match of molecular surfaces of the rotating and static components, that we called ‘rotor-stator property’. We showed that rotor-stator systems can be formed with C_{60} and higher fullerenes too and also with disubstituted cubane derivatives. At elevated temperature a single phase copolymerization occurs induced by the thermal decomposition of cubanes.

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Keywords: *fullerenes; topochemistry; cocrystals;*

P-0747

SYNTHESIS AND STRUCTURE OF A SULFONATO-BRIDGED TI-OXO CLUSTER

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Transition metal -oxo clusters find increasing interest in material science as nanosized building blocks, especially for inorganic-organic hybrid materials[1]. When polymerizable ligands are attached to the cluster surface, the inorganic building blocks can be incorporated in polymers by covalent bonding[2]. Numerous transition metal-oxo clusters with polymerizable ligands were synthesized and used to obtain polymers with tailored properties.

A versatile route to such clusters is by reactions of transition metal alkoxides with carboxylic acids, whereby cluster size and shape is determined by the alkoxide/acid ratio, the kind of carboxylic acid and the kind of alkoxo groups.

During the last decade mainly carboxylic acids were used for cluster synthesis. The change from bidentate carboxylic acids to potentially tridentate ligands for the cluster synthesis can widen the range of structural possibilities.

In this work we present the synthesis and structure of a new type of Titanium-oxo cluster based on phenylsulfonic acid.

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Keywords: *Oxo Cluster; Hybrid materials;*

P-0748

SYNTHESIS AND CHARACTERIZATION OF CADMIUM TELLURIDE NANOPARTICLES

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Cadmium telluride is an attractive semiconducting material. Its unique properties are making it an ideal candidate for applications in optoelectronical devices (mainly solar cells). In this work we present a new method of synthesis of cadmium telluride using bis(diphenylphosphino)amine, cadmium carbonate and tellurium as starting materials.

In our system, all three reactants are suspended in toluene and heated in an autoclave to 160 – 180 °C. Under these mild conditions acidic H^+ from NH group of $Ph_2PNHPPh_2$ protolyses cadmium carbonate releasing cadmium(2+) ions. In addition P(III) atoms of $Ph_2PNHPPh_2$ also act as reducing agents reducing tellurium to telluride. That means that cadmium telluride is directly formed in the reaction mixture and no other interventions into the system are necessary.

Formation of CdTe was confirmed by PXRD analysis. Product morphology was investigated by SEM imaging. Particle size of prepared CdTe is about 10^2 nm, however, particle size distribution is not narrow and formed particles are aggregated. We are studying this problem intensively.

To conclude, we offer a new method of synthesis of cadmium telluride using $Ph_2PNHPPh_2$, $CdCO_3$ and Te as starting materials. Main advantage of presented system is that the whole reaction takes place in one reaction step.

Keywords: *Nanoparticles; Cadmium telluride;*

P-0749

PREPARATION AND CHARACTERIZATION OF POROUS ALUMINA SOL-GEL COATINGS

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Nowadays there is a growing interest in sol-gel coatings since sol-gel process provides a relatively cheap, simple and robust method to create thin films on solid substrates giving them special features (antireflexion, self-cleaning etc.).

Our aim was to determine experimentally the optimum conditions (precursor sol composition, rate of film transfer) for preparing γ-Al_2O_3 coatings with maximum porosity via a sol-gel process applying surfactant templates. Thickness and refractive index of the coatings were characterized by UV-Vis spectrophotometry and scanning angle reflectometry analyzing the data with different optical models[1–3]. Porosity was estimated with the Lorentz-Lorenz formula.

A modified recipe[4] was used for the precursor sols which were prepared via the hydrolysis of aluminium-triisopropoxide, the acidic peptization of the boehmite formed and the addition of cetyl-trimethyl-ammonium-bromide (CTAB) as template. Thin films were prepared on microscope glass slides by dip-coating. The coated substrates were dried and annealed at 500 °C for 90 minutes. The analysis of differential scanning calorimetry, thermogravimetry, infrared spectroscopy and wide-angle X-ray scattering proved that this annealing process results in γ-Al_2O_3 powder.

An optimum CTAB concentration was established at which porosity of ca. 40 % was reached. The highly porous samples can be good candidates for sensor applications in the future.

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Keywords: *sol-gel processes; thin films; UV-Vis spectroscopy; nanotechnology;*

P-0750

SOLUTION-PROCESSED ULTRATHIN CHEMICALLY DERIVED GRAPHENE FILMS AS SOFT TOP CONTACTS FOR SOLID-STATE MOLECULAR ELECTRONIC JUNCTIONS

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A major goal of molecular electronics is to understand charge-transport properties of single molecules and their ensembles. Ultimately this will pave the way for electronic components made of molecular building blocks that can overcome the limits of conventional semiconductor technology.[1, 2] Compared with the junctions built on a very limited number of molecules, self-assembled monolayers (SAMs) offer a more reproducible way for the fabrication of molecular electronic devices, and are more amenable to mass production and integration. However, direct in situ evaporation of metals onto SAMs has proven to be too invasive and damaging. Filamentary paths of metals or damages to the molecules can very easily cause short-circuits.

Here, we report the use of solution-processed chemically derived graphene (CDG) films for non-destructive fabrication of molecular electronic junctions.[3] Wafer-scale continuous films with sub-10 nm thicknesses can be uniformly delaminated from the substrate and transferred without polymer supports onto SAMs to function as soft electrical top-contacts. Two types of molecular junctions are developed demonstrating a versatile application of the CDG thin-films. We believe this protocol will greatly enrich the test beds for molecular electronics due to its low-cost, easy-processing and flexible nature.

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Keywords: *Molecular electronics; Graphene;*

P-0751

ORGANIC NANOTUBES FOR DRUG LOADING AND CELLULAR DELIVERY

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Background: Organic nanotubes made of synthetic amphiphilic molecules are novel materials that form by self-assembly.

Objectives: Organic nanotubes were expected to apply a drug carrier in drug delivery system.

Methods: Organic nanotubes with a carboxyl group (ONTs) at the surface were used as a carrier for the anticancer drug doxorubicin, which has a weak amine group. Drug loading into ONT and cellular delivery of them was investigated, using cytotoxicity and transmission electron microscope.

Results: The IC(50) values of ONT for cells were higher than that of conventional liposomes, suggesting that ONTs are safe. The results showed that the drug loading of ONTs was susceptible to the effect of ionic strength and H(+) concentration in the medium, and drug release from ONTs was promoted at lower pH, which is favorable for the release of drugs in the endosome after cellular uptake. ONTs loaded with the drug were internalized, and the drug was released quickly in the cells, as demonstrated on transmission electron microscopy images of ONTs and the detection of a 0.05% dose of ONT chelating gadolinium in the cells. Moreover, ONT could be modified chemically with folate by simply mixing with a folate-conjugate lipid.

Conclusion: These novel, biodegradable organic nanotubes have the potential to be used as drug carriers for controlled and targeting drug delivery.

Keywords: *nanotube; cellular uptake; drug load; doxorubicin;*

P-0752

DNA-NANOCUBES HYBRIDS FOR BIOMOLECULAR RECOGNITION

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Biomolecules recognition is a very important area of research for medical diagnostic improvement. Among existing methods, the specific disassembling of network based on “aptamer” – DNA interactions appears to be one of the most promising strategy. Aptamers are oligonucleic acids or peptides selected through repeated rounds of in vitro selection (SELEX: systematic evolution of ligands by exponential enrichment) to bind strongly to various molecular targets such as proteins, nucleic acids and even whole cells. Combined with a complementary sequence, oligonucleotide aptamers are able to assemble owing to Watson-Crick DNA base pairing. The obtained double strands disassemble as the target molecule is introduced, aptamer-target interactions being higher than that of aptamer-complementary sequence. While aptamers are bonded to nanoparticles, self-assembled networks of nanoobjects can be obtained. Their disassembling in the presence of the target molecule can strongly disturb the physical properties such as plasmonic or magnetism, depending on the chemical nature and the organization of nanoparticles. Such physical disturbing can be easily exploited for biomolecular detection. In this context, we develop nanohybrids composed of DNA associated with platinum, iron-platinum or iron oxide nanocubes. Since they own planar faces, nanocubes represent unique shapes for self-assembly. The poster will present all aspects of this work: the chemical synthesis of nanocubes, the ligands exchange to confer water solubility and to further introduce specific functions, and the peptidic coupling between DNA and functionalized nanocubes.

P-0753

POLYMER NANOPARTICLES FOR THE CONTROLLED RELEASE OF SINGLET OXYGEN

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Singlet oxygen ($^1O_2$) is a reactive form of O_2 that plays an important role in many oxidation processes, e.g. photooxidation, DNA damage, and photodynamic therapy[1]. Due to its short lifetime and often low local concentration of ground state O_2, a controlled production and release of $^1O_2$ is difficult to achieve. In this work we describe a new strategy for producing singlet oxygen, using the thermolysis of 9,10-diphenylanthracene (DPA) endoperoxides incorporated within polymer nanoparticles. DPA can react reversibly with singlet oxygen, forming an endoperoxide that can regenerate the initial aromatic compound by thermolysis, releasing singlet oxygen[2].

Nanoparticles of polybutylmethacrylate were prepared by a two-step, starved feed emulsion polymerization technique, using a DPA-acrylate co-monomer. The nanoparticles were then irradiated in the presence of a photosensitizer to obtain the endoperoxides. Subsequent thermolysis of the nanoparticles triggers the controlled released of singlet oxygen. We will present the preparation and characterization of the nanoparticles as well as the comprehensive fluorescence spectroscopy study of endoperoxide formation and thermolysis in the nanoparticles.

Acknowledgement: *SM was supported by a Ph. D. grant from FCT- Fundacio para a Ciencia e Tecnologia (SFRH/BD/47660/2008).*

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Keywords: *Singlet Oxygen; Nanoparticles; Polymers;*

P-0754

COVALENT POLYOXOMETALATE HYBRIDS FOR THE ELABORATION OF FUNCTIONAL DEVICES

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Polyoxometalates (POMs) are molecular oxides offering a wide range of applications in catalysis, medicine and materials science. The modularity of their structural and electronic properties associated with their ability to accept electrons or the diversity of their functionalization ways, make them attractive candidates for the elaboration of multifunctional molecular materials. The Polyoxometalates group in Paris has a long tradition in the synthesis and functionalization of organic/inorganic hybrids based on POMs, especially by anchoring a covalent link between the polyanion and the organic tether.[1] This covalent approach allows us to initiate new applications for POMs by integrating them into functional devices and strengthening the interaction between the organic and the inorganic part. Based on recent examples,[2, 3] we will herein present the synthetic approach towards various functionalized POMs and the applications of the resulting hybrids in different fields such as artificial photosynthesis,[4] molecular nanosciences[5] or self-organized materials.[6]

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Keywords: *Polyoxometalate; Molecular electronics; Supramolecular chemistry;*

P-0755

A SAMPLE CHEMICAL ROUTE TOWARD MONODISPERSE IRON CARBIDE NANOPARTICLES DISPLAYING TUNABLE MAGNETIC AND UNPRECEDENTED HYPERTHERMIA PROPERTIES

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Monodisperse and air stable magnetic nanoparticles displaying high magnetization and tunable anisotropy are highly desirable for several nanotechnology applications[1]. However, among the various magnetic nanoparticles previously described, no one fills of these properties. A recent study in our group reveals that iron(0) nanoparticles could be good candidates for hyperthermia but lack the air-stability criteria[2]. In contrast, iron/iron oxide core-shell and iron oxide nanoparticles display a good air-stability but a low magnetization. An improvement of these behaviors requires either coating iron(0) nanoparticles with a protective shell or changing the chemical nature of the particles[3]. In this respect, iron carbides nanoparticles are particularly attractive since combining high magnetization, air stability and the possibility to modulate the magnetic properties as function of carbon content. But up to now no wet chemical methods for their synthesis were described.

Here, we report the first chemical synthesis sample and reproducible for the preparation of monodisperse iron carbides and iron/iron carbides nanocrystals with controlled sizes and compositions[4]. The synthesis deriving from the Fischer Tropsch mechanism is original and is based on decomposition of $Fe(CO)_5$ on different mild conditions on a colloidal solution of iron(0) NPs stabilized by hexadecylammonium chloride and hexadecylamine[5]. Under dihydrogen atmosphere, we were able to enlarge the particle size and activate the carbon diffusion inside the iron nanoparticle. Their mean size is well controlled by adjusting the seeds one and/or the $Fe(CO)_5$ concentration. All these nanoparticles display excellent magnetic properties and air-stability. More, by tunning the experimental conditions, as temperature and reducing agent, we can control the amount of carbon diffused inside and therefore their magnetic anisotropy.

However, these nanoobjects have no precedent and some of them display the highest efficiency so far reported for magnetic hyperthermia in the current operating treatment conditions.

Keywords: *nanoparticles; magnetic properties;*

P-0756

PREPARATION OF PEROVSKITE OXIDE THIN FILM ELECTRODES BY RF MAGNETRON SPUTTERING FOR ENVIRONMENTAL APPLICATIONS

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The search of new and more efficient methods for the treatment of effluents containing several persistent pollutants species is a very important issue. Electrochemical technology offers an efficient and environmental friendly approach for the elimination of different kinds of pollutants. The removal of metallic ions from solution by electrochemical reduction is a well known process. Depending on the cathode material and applied potential, a selective recovery of metals from solution can be performed.

Perovskite type structure oxides are potential materials for this application. However, special attention must be given to the electrode construction, in particular its mechanical stability. The sputtering technique presents several advantages on electrodes preparation[1] such as high deposition rates, high-purity films and extremely high adhesion film/support.

The main objective of this work was to optimize the growth conditions for obtaining crystalline $Ca_{1-x}Sm_xMnO_3$ thin films prepared by an innovative approach using the magnetron sputtering technique. The films were prepared by radio frequency magnetron sputtering under various deposition conditions using nanosized powder compacted targets. The polycrystalline samples $Ca_{1-x}Sm_xMnO_3$used as targets were previously prepared by self-combustion method using citric acid[2]. The plasma medium was characterized using optical emission spectroscopy.

The characterization of the bulk and the thin films were performed using different tools. The structural and morphological characterization was carried out by X-ray diffraction (XRD), scanning electron microscopy (SEM) and atomic force microscopy (AFM).

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Keywords: *Perovskite phases; Thin films; Nanotechnology; Surface analysis; X-ray diffraction;*

P-0757

COATING PT(O) NANOPARTICLES WITH METHYLS: THE REACTION BETWEEN METHYL RADICALS AND PT(O)- NP(S) SUSPENDED IN AQUEOUS SOLUTIONS

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Methyl radicals react with Pt^o-NPs suspended in aqueous solutions in fast reactions. The major product is stable methyl coated Pt^o-NPs, $(Pt^o\text{-NPs})\text{-}(CH_3)_n$. C_2H_6, C_2H_4 and some polymerization products are also formed. These results differ significantly from those reported for the analogous reactions with Ag^o and Au^o NPs. The source of the differences is discussed in detail.

Keywords: *Pt(0); ; Nanoparticles; ; Methyl Radicals;*

P-0758

END-TO-END DISTANCE DETERMINATION IN A CUCURBIT[6]URIL-BASED ROTAXANE BY PULSED ELECTRON-ELECTRON DOUBLE RESONANCE SPECTROSCOPY

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The development of molecular machines is one of the most attractive and challenging fields of supramolecular chemistry. In particular, there is a great interest in their potential use for nanoelecronics and nanotechnology.[1]

For an efficient design of such nanostructures, it is required a quantitative knowledge about the structure, features and properties of each of its molecular components, as well as for understanding of the mechanical and dynamic properties once these nanoobjects are assembled together in a supramolecular architecture. The access to the information regarding the intrinsic, structural and conformational flexibility of these molecular machines can be gained from the distance distribution among their constituting objects.

In 2011, we have reported the synthesis and the characterization of a series of paramagnetic cucurbituril-based rotaxanes, in which the thread end-units were constituted by 2,2,6,6-tetramethylpiperidine-N-oxyl (TEMPO) radicals.[2]

Here we report the use of pulsed electron-electron double resonance (PELDOR) spectroscopy for the determination of the distance distribution among the nitroxidic end units of a paramagnetic cucurbit[6]uril-based [3]rotaxane (**1**).[3]

PELDOR measurements on rotaxane (**1**) have revealed a very sharp distances distribution, centered at 3.07 (± 0.14) nm that can be attributed to the elongated conformation inferred by the cucurbit[6]uril macrocyclic units. In the absence of the latters, the free thread exhibited a broader and more complex distance distribution underlining a higher conformational freedom.

These experimental data have been also strongly supported by molecular dynamic simulations.[3]

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Keywords: *EPR spectroscopy; Radicals; Rotaxanes; Supramolecular Chemistry;*

P-0759

HIERARCHICAL SELF-ASSEMBLY OF LUMINESCENT LANTHANIDE COMPLEXES ON SILICON

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An innovative approach for surface functionalization with Lanthanide complexes via molecular recognition is presented. Silicon wafers were decorated with tetraphosphonate cavitands using photochemical grafting protocol to obtain a functional surface presenting specific molecular recognition properties.[1] This kind of cavitands are known as versatile synthetic receptors which can complex neutral molecules like alcohols[2] as well as positively charged species like ammonium salts.[3] Based on this premise, we decided to functionalize the phenanthroline ligand of luminescent Eu complex with a suitable substituent bearing a methyl ammonium unit. Ternary complex formation in solution was confirmed by NMR and MS experiments. Photophysical studies revealed good luminescence properties of complex (quantum yield 20%) and also confirm complexation. A slightly modified protocol has been used for solid state transfer. Deposition of ternary complex on silicon wafers consists of two steps: host-guest complexation of phenanthroline-sarcosine ligand followed by coordination of $Eu(hfac)_3$. Each step was monitored by XPS technique and physisorption has been excluded. The resulting hybrid material presents good luminescent properties without luminescence quenching caused by the silicon surface.

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Keywords: *Lanthanides; Supramolecular chemistry; Molecular recognition; Cavitands; Silicon;*

P-0760

PSEUDOROTAXANES AS PROTOTIPES OF MOLECULAR MACHINES WORKING ON GRAPHITE SURFACES

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Nanoscience is rapidly expanding its influence on our daily life; this is probably due to the advantages of new technologies based on the molecular behavior of nano-sized systems. Supramolecular self-assembled systems as rotaxanes, pseudorotaxanes and catenanes, are depicted as some of the most promising molecular structures in the development of nanosciencies, because they are good prospects for building molecular machines. In this work, we deal with pseudorotaxanes, which are systems composed of two interpenetrated molecules -axle and wheel-, attached to graphite surfaces. The axles we have synthesized and characterized are viologen derivatives; they were designed to have a recognition site for a disulfo-dibenzo-24-crown-8 ether and also a carboxilate group, that can be used to electrochemically attach the axle to a graphene surface. The axles and its dynamical behavior in solution with the wheel have been characterized by several techniques such as nuclear magnetic resonance, electronic spectroscopy and mass spectrometry. In this work, we will present our results on Molecular Dynamics simulations using AMBER 11 and also Potential of Mean Force (PMF) calculations. The simulations have shown that two co-conformations are possible for the associated components in solution, one is the traditional threaded co-conformation and the other one is the exo-associated co-conformation, better known as the taco co-conformation. The PMF results prove that a recognition site for the wheel is present in the axle, that is located close to the cationic nitrogen on the axle. The linkage between the axles and a graphene sheet was studied from first principles calculations using the Density Functional Theory. This results show that a covalent bond between the axle and the graphene surface can be formed.

Keywords: *Supramolecular chemistry; Nanotechnology; Electrochemistry; Ab initio calculations; Molecular Dynamics;*

P-0761

DEVELOPMENT OF VESICLE-BASED CHEMOSENSORS: DIRECTED FUNCTIONALIZATION OF VESICLE SURFACES

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For the development of highly specific vesicle-based chemosensors, a well defined two-dimensional assembly of different binding sites on the spherical vesicle surface is necessary. However, simple addition of the desired receptors to the phospholipid mixture during vesicle preparation is subject to restrictions: Firstly, suitable artificial amphiphilic receptor molecules are needed – often only accessible by a tedious synthesis. Secondly, based on previous works from our group, the embedded binding sites are supposed to gather in tightly packed patches due to phase separation.[1] This makes a directed receptor assembly on the surface difficult. In order to overcome those limitations, our approach relies on a subsequent controlled attachment of receptors on unfunctionalized liposome membranes, which are only modified with special binding anchors. As a fast and reliable reaction for covalent fixation, the UV light induced thiol–ene click reaction is used. This reaction fulfills the essential requirement of water and oxygen tolerance and exhibits biocompatibility. Here, we present preliminary results from our investigations towards a defined receptor structuring on vesicle surfaces.

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Keywords: *Supramolecular chemistry; Molecular recognition; Vesicles; Sensors; Click chemistry;*

P-0762

‘MOLECULAR CLIP’ RECEPTORS FOR DIHYDROXYBENZENES WITH SUITABLE BINDING SITES FOR ENHANCED COPPER COMPLEXATION

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Urea-based Molecular Clips mimic natural receptors, with an upper organic-cavity that binds to dihydroxybenzene (DHB) molecules.[1] Many neurotransmitters such as dopamine contain a DHB moiety.

The locking phenyl groups of the Molecular Clip hold it in a convergent conformation for binding a DHB, but these groups – with suitable modification can also serve as a binding site for metals. The addition of nitrogen-containing groups here are ideal for copper complexation[2], whose ions play a large role in neural functions. Elevated Cu2+ levels have been implicated in the formation of protein plaques that are found in the neural tissue of Alzheimer’s patients.[3] Such clips may act a model for the binding and control of the redox states of copper, and protection of DHB-type neurotransmitters.

Current work involves the addition of bipyridine moieties to the lower locking phenyl ring system, and synthesis of new benzil molecules which can be further functionalised to enhance copper complexation.

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Keywords: *Supramolecular chemistry; Molecular recognition; Dopamines; Copper; Allosterism;*

P-0763

HIGH-LEVEL GEOMETRIC CONTROL OF NEW ROTAMERIC MOLECULAR CLIP RECEPTORS: NMR STUDIES OF ROTAMER INTERCONVERSION AND BINDING TO DIHYDROXYBENZENE GUESTS

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Molecular clips, originally introduced by Nolte[1], are well-known artificial receptors for dihydroxyaromatics, e.g. resorcinol, catechol, catecholamines, and other biomolecules bearing a dihydroxyaromatic unit. Two xylylene walls and two carbonyl groups, making a pre-organized cavity, are the key features which bind the substrate via two aryl-stacking & two hydrogen-bonding interactions.[1]

We have prepared new clips which exist as rotamers: isomers interconverted by rotation about a single bond.[2] The rotameric site is incorporated into two phenyl substituents which control the convergent conformation of the receptor, but do not directly disturb the binding site.

VT-NMR allows us to interconvert these rotamers, and measure the energy barrier; the latter is also accessible via free energy calculations. Surprisingly, the energy barrier was found to be independent of the nature of the substituent in the 3,3'-positions, but this has now allowed us rationalize the mechanism of interconversion.

We have now moved on to a more hindered 2,2'-disubstituted series, where variation of the substituent now allows a significant biasing towards the trans-rotamer being more stable (up to 100%), and also leads to higher interconversion barriers.

NMR titration yields binding constants to guests such as resorcinol.

The new rotameric clips show considerable promise for high-level control of receptor geometry and of associated binding of guests to each rotamer.

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Keywords: *Molecular recognition; NMR spectroscopy; Isomerization; Atropisomerism; Host-guest systems;*

P-0764

NANOPARTICULATE AEROSOL MANUFACTURING PROCESS

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Micronised drug particles for MDI products of aerosol asthma drugs on the market tends to be acculumated on the inner surface of containers, or valve components during their shelf lifes. These micronised particles can also undergo moisture initiated instability where water can promote chemical instability and particle adhesion/cohesion differences in these formulations.

While we were devoloping a new aerosol formulation, suprisingly, we founded that if the formulation have specific parameters in terms of particles size distribution rate or morphology which affects obtainable surface area and moisture absorbtion profiles, the resulted formulation have greater suspension stability in its life-time use while comparing its former specifications.

The formulation must be a nanoparticulate pharmaceutical composition -solid concentration between 0.1 % – 0.5 %- at least one active pharmaceutical ingredient or salt or solvate, at least one propellant or propellant mixture, at least one polymer or polymer combination which has moleculer weight of 190-70000 g/mol.

Formulation trials have been done for these nanoparticulate aerosol formulations in order to obtain desired particle size and morphology which are < 0.5 μm and spherical, respectively. Sample concentrations were used in 2.5 % – 5 % (as weight basis). Solution or suspension were prepared in water and mixed by mechanical mixer before spraying through the nozzles. Nano spray-drying method encapsulates successfully active ingredient with polymer/ polymer combinations which increases the moisture and gas barrier properties while increasing surface area of dispersed particles in liquefied gas. This leads to improvements on the chemical instability resulted from the moisture in the structure and more cohesive forces which enhances the uniformity of the composition. Active ingredient were mixed with polymer or polymer combinations in different ratios. A yield of 70-75% is attained with the use of spheric particles with the size between 0,6 and 4 micron.

Keywords: *nanoparticles; Drug delivery; Polymers; Nanotechnology;*

P-0765

ELECTRON AND PHONON SIZE-QUANTIZATION EFFECTS IN NANOSTRUCTURED ZINC SELENIDE THIN FILMS. OPTICAL ABSORPTION AND RAMAN SCATTERING STUDY

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Nanostructured thin films composed by close packed zinc selenide quantum dots of sphalerite structural type were synthesized by our recently developed template-free chemical route. Structural and compositional characteristics of the films were studied by X-ray diffraction. Average crystal size, lattice constants, lattice strain and dislocation densities were computed by analysis of the XRD data for as-deposited and thermally annealed films. Electronic quantum confinement effects in the synthesized quantum dot solids were investigated by optical absorption spectroscopy. On the basis of the measured spectral dependencies of absorption coefficients of the films, band gap energies were calculated with a combined interpolation-extrapolation technique, employing the parabolic approximation for the dispersion relation. The experimentally measured dependence of the band gap energy of the films on the average crystal size was compared to the predictions of various theoretical models. To study the phonon-confinement effects in the synthesized low-dimensional semiconductors, Raman scattering technique was employed. Raman spectra were recorded using micro-Raman spectrometer, Horiba Jobin-Yvon LabRam 300, equipped with double-frequency Nd:YAG laser line operating at 532 nm. The band due to the LO phonon mode in the Raman spectra of the synthesized quantum dot solids was found to exhibit a notable red shift in comparison to the value characteristic for the bulk material. The half-width of this band was found to be significantly larger in the case of the studied low-dimensional solid as compared to the bulk sample, and its low-frequency side exhibited a pronounced asymmetry. These effects were attributed to the relaxation of the $k=0$ selection rule, due to the finite dimensions of the quantum dots. The low-frequency shoulder of the one-phonon LO band could be attributed to the surface optical phonon (SO) or zone-edge (ZE) modes. Aside from the one-phonon LO mode, also several replicas thereof have been detected in the Raman spectrum.

Keywords: *zinc selenide; quantum dots; phonon confinement effects;*

P-0766

HYDROGEN IN LIGHT-METAL CLUSTER-CAGE ASSEMBLIES: TOWARDS A NANOFOAM STORAGE

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Potential high-capacity storage of hydrogen in metal-hydride solids is problematic due to hydrogen strongly binding to metal atoms, with its release requiring unacceptably high temperatures. Adsorption of hydrogen on metal-cluster surfaces impose similar limitations, while hydrogen absorption into cluster cages may enable its relatively easy withdrawal due to predicted lower stability of the systems.

This work presents results of ab initio calculations for main-group light-metal clusters M_n ($n \leq 18$) with up to two endohedral H_2 molecules [*J.Phys.Chem.A* 115 (2011) 12105]. Of primary interest are the systems structure and stability relative to separate cage and H_2 molecule(s), including energy barriers to hydrogen escape from the cage. The origin of the reduced stability is explored, involving cage-molecule charge-transfer and Coulomb explosion of the molecules confined inside the surrounding cage. Related potential direct energy storage is also discussed.

Preservation of the cage integrity and hydrogen confinement are investigated for these core-shell units merging together into larger aggregates. Such cluster assemblies structurally resemble fragments of hydrogen-filled metal nanofoams, possible isomeric forms of metal-hydride solid, nonfilled (pure-metal) nanofoams being already feasible experimentally. With H_2 molecules undergoing metal-cage induced (endohedrally catalyzed) dissociation, different "nanofoam" isomers are composed of either pairs or single H atoms suspended electrostatically inside the metal cage units ("nanobubbles"). Interesting features include simultaneous exit of two H atoms, unexpected stabilization of the systems in specific geometries, higher stability of assembly isomers formed by less stable isomers of units. Preliminary structural extrapolations estimate potential hydrogen storage capacity of up to ~10 weight-%.

Also of interest is the alteration of the metal-cage structure and related properties via inserting hydrogen, including induced polarity. Non-covalent interactions of the molecular core and the metal shell can facilitate metal-cluster shape and property design and tuning. Relevant parameters characterize charge distribution, electronic excitation, ionization, and electron attachment.

Keywords: *Hydrogen; Cluster compounds; Cage compounds; Main group elements; Computational chemistry;*

P-0767

SYNTHESIS AND CHARACTERIZATION OF SELECTIVE SENSOR NANOPARTICLES FOR MAGNETIC RESONANCE IMAGING

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The aim of the present study is the synthesis of iron oxide nanoparticles functionalized by hyperbranched sulfated polyglycerols (a heparin analogue) on their surface. This leads to antiinflamatory, antimetastatic, antiathereosclerotic, and antiproliferativ effects in organisms and can accumulate in infected biological tissue. These hyperbranched sulfated polyglyceroles functionalized iron oxide nanoparticles might be used as contrast agents in the magnetic resonance imaging. It is found that the number of functionalizing groups in the hyperbranched sulfated polyglycerol determines the stability of the iron oxide nanoparticles. Measurements are performed in different biological media, such as Dulbecco`s Modified Minimum Medium (DMEM) and isotonic saline, where the stability of the nanoparticles and aggregation is probed. Additionally, cell viability studies are reported using human colon cancer cells. These are incubated with hyperbranched sulfated polyglycerol functionalized iron oxide nanoparticles, indicating that the viability of the cells is increased. Surface plasmon resonance (SPR) studies indicate that the hyperbranched sulfated polyglyceroles functionalized iron oxide nanoparticles lead to an inhibition of L-selectin binding. Finally, the binding of hyperbranched sulfated polyglycerol functionalized iron oxide nanoparticles to infected tissue is tested using a mice-model, which is infected with viral induced myocarditis.

These results indicate that hyperbranched sulfated polyglycerol functionalized iron oxide nanoparticles may be suitable for being used as a contrast agent in the magnetic resonance imaging.

Keywords: *Nanoparticles; Inflammation; Inhibitors;*

P-0768

MOLECULAR ELECTRONICS IN SELF-ASSEMBLED AND SOLID-STATE DEVICES

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Molecular nanogap junctions have been the subject of intense study for the last decade, and include a variety of approaches, such as mechanically controlled break junctions, electromigration and scanning probe techniques. Herein, we report recent progress towards the fabrication of novel self-assembled molecular electronics systems, including solid-state devices [1, 2] and chemically prepared nanogap junctions [1].

Self-assembled solid-state monolayer devices containing a range of conjugated organic molecules have been realized employing chemically derived graphene as a soft, transparent top-contact. Additionally, the graphene can serve as a protecting layer against monolayer degradation from evaporating a metallic top electrode [1]. Finally, chemically prepared nanogaps between gold nanostructures have been achieved in solution [3] and on surfaces [4] with a variety of molecules trapped in the gaps, providing a possible route towards large-scale fabrication of (single) molecular devices.

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Keywords: *Molecular electronics; Self-assembly; Nanostructures; Graphene;*

P-0769

QCM STUDY OF SAM FORMATION ON SILVER NANOROD LAYERS

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Self assembled monolayers (SAM) of thiols and disulfides have been studied for their potential application, since their discovery in 1983 by Nuzzo and Allara. SAM formation provides one easy route towards surface functionalization by organic molecules (both aliphatic and aromatic) containing suitable functional groups like –SH, –CN, –COOH, $–NH_2$ and silanes on selected metallic (Au, Cu, Ag, Pd, Pt, Hg and C) as well as semiconducting surfaces (Si, GaAs, indium coated tin oxide, etc.) [1].

Electron transfer through nanometer-thick organic films is of fundamental importance in the development of nanometer-scale electronic materials. Knowledge of how chemical compositions and chemical structures affect electron transfer between a solid substrate and a redox-active molecule is central to the study of molecular-level electron transfer[2].

The adsorption of SAM was monitored using a quartz crystal microbalance (QCM). QCM measurements confirmed the inhibition of molecules adsorption on substrate surface[3].

The aim of this study was modification of silver nanorod layers electrochemically deposited on stainless steel substrate with SAM. The effect of time and concentration of 1-hexadecanethiol in chloroform solution on the formation of SAM adsorbed on silver nanorod layers was studied using QCM. It was found that the prolonged time of adsorption step resulted in the SAM molecular weight increase.

Acknowledgement: *This work was supported by the Grant VEGA 1/0211/12 of the Slovak Scientific Grant Agency and the Project APVV SK-CZ-0113-11 of the Slovak Research and Development Agency.*

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Keywords: *nanostructures; self-assembly; monolayers; silver; electrochemistry;*

P-0770

ACTUATING PROPERTIES OF COMPOSITES CONTAINING CARBON NANOTUBES

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The composites with elastomeric matrix are highly developing, because of various interesting applications. Carbon nanotubes (CNT) have been widely used as filler for different kinds of polymers for the preparation of high performance composite materials. Recently, nanotube-enriched elastomeric polymers have shown photo-actuating properties. Photo- and thermo-mechanical actuation is preferred to electromechanical transduction because of some advantages including wireless connection, a producing low noise, fast response, etc. However, only few materials actually exhibit photo or thermal-actuation. This presentation will contribute to solving basic aim of 7 RP project NOMS (Nano-Optical Mechanical Systems) which is the processing of photoactuating elastomeric composites containing well dispersed carbon nanotubes. The purpose of the project is to build a visual-aid tablet for visually impaired people.

For preparation of the composites ethylene vinyl acetate copolymer – EVA was used as polymeric matrix. Two different types of CNT, multiwall CNT, and singlewall CNT were use as fillers. Non-covalent modification of CNT was carried out with the surfactant based on pyrene molecules. The nanocomposites were prepared by casting from solution. The actuation of two forms of the nanocomposites, strips and specifically designed samples prepared using so called punch and die system was study. The dispersion of CNT in the polymeric matrix has been investigated by scanning electron microscopy and transition electron microscopy. In order to characterize the deformation changes of material under light irradiation, Nanoindenter TI-750 (Hysitron, USA), and SEM technique combined with camera were applied for study of light inducted photo and thermo-actuation of prepared nanocomposites.

In the presentation we will show results of photo-actuating behaviour of new photo-actuating materials based on the commercial elastomers such as ethylene-vinylacetate copolymer filled with carbon nanotubes.

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Keywords: *actuator; polymeric nanocomposite; carbon nanotubes;*

P-0771

NANOTECHNOLOGY OF MOLECULAR LAYERING FOR PREPARATION OF TRADITIONAL AND MEMBRANE CATALYSTS

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Molecular layering method (ML) is based on the irreversible interaction between of low-molecular reagents and functional groups of a surface of solid substrate under the conditions of continuous reagent input and removing the formed gaseous products. In this multistage process, a number of physical and chemical stages are separated; as a result of these stages, a monomolecular layer of new structural units is formed on the matrix surface. The thickness of the deposited coating is controlled by the number of ML cycles rather than the exposure time. In this case the precision in determining the composition is achieved on the atomic–molecular level.

In the present study the series of nanostructured catalysts was prepared by ML deposition of Ti, V oxides structures on the alumina powders. The other application of ML was the optimization of the selectivity of gas permeability of alumina membranes by modification of their porous structure with ML deposition of titania into pores of initial membrane at a variation of number of cycles ML. The following insertion by ML method of the vanadium - and vanadium-phosphorus oxide nanostructures gave the composite membranes catalytically active in oxidative dehydrogenation of methanol to formaldehyde. It was shown that methanol conversion and selectivity of formation of formaldehyde on traditional and membrane catalysts depend on the nature of the catalytically active components on a surface of modified catalyst and on the number of ML cycles.

It is shown that the nanotechnology of ML gives a possibility to prepare on the surface of porous support in the united chemical-technological cycle the assembly of nanostructures of various functional purpose: for providing the system with the desired catalytic properties and for the regulating of the pores size of substrates.

Keywords: *molecular layering; membrane; catalyst; oxidative dehydrogenation;*

P-0772

EFFECTS OF MONTMORILLONITE-SORBITOL ON CRYSTALLIZATION BEHAVIORS AND IMPACT RESISTANCE OF POLYPROPYLENE NANOCOMPOSITES

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Effects of sorbitol-modified montmorillonite (MMT-sorbitol) on crystallization behaviors and impact strength of polypropylene (PP) nanocomposites were studied. The modification process included mixing MMT and sorbitol at a MMT/sorbitol weight ratio of 1/2 using a high speed mixer. Results from X-ray diffraction (XRD) indicated that sorbitol was intercalated between MMT layers along the 001 direction. PP resin was mixed with MMT-sorbitol powder at 1 to 7 parts per hundred of resin (phr) by means of melt blending on a two-roll mill, and pressed into specimens. XRD patterns indicated that PP chains could intercalate into the gallery of MMT-sorbitol to form exfoliated PP nanocomposites. The crystal obtained from this process was the α-monoclinic PP form. Compared to the neat PP, higher amounts and smaller sizes of spherulites were observed in the nanocomposites. Specimens of the nanocomposite with a MMT-sorbitol concentration of 1 phr exhibited the highest impact strength: 3.4, 3.2 and 2.7 kJ/mm^2 when the specimens were at room temperature (25 °C), 0 °C and -30 °C, respectively.

Keywords: *Crystallization behaviors; Impact resistance; Montmorillonite-sorbitol; Polypropylene;*

P-0773

ROTOR-STATOR COCRYSTALS OF FULLERENES WITH CUBIC AND OCTAHEDRAL MOLECULES

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Fullerenes form cocrystals with a great variety of organic molecules. The majority of these materials belongs to various host-guest systems, depending on the shape and size of the counter molecules. Fullerene-cubane cocrystals represent a special family: none of the components form a host framework, they rather form separated sublattices[1]. The major stabilizing factor of such structures is the almost perfect mach of the molecular surfaces of convex fullerenes and concave cubanes. The expanded fullerene sublattice confines cubanes in static positions. On the other hand, the atomic arrangement of the fullerene surface is incommensurate with that of cubane, therefore, the rotation of fullerenes has no influence on the match. Thus, cubanes behave as a molecular bearing for the freely rotating fullerene, resulting in unusual dynamics. The alternating array of static and rotating components distincts this family of rotor-stator phases from both the orientationally ordered and plastic crystals. Rotor-stator properties slightly depend on the size and symmetry of the fullerenes and the substituents of cubane, but the major properties are characteristic of the whole family. We present here a new member of this family, the rotor-stator cocrystal of the endohedral $Sc_3N@C_{80}$ with cubane. In this material the rotor-stator properties of the molecules are extended to the rotation of the endohedral Sc_3N units. Besides the cubic shaped cubane, octahedral and other high-symmetry molecules may form similar cocrystals with fullerenes. In the absence of octahedral molecules of suitable size, we studied the fullerene cocrystals with the distorted octahedral pairs of mesitylene. We compare the influences of the cubic and octahedral shapes on the structures and properties.

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Keywords: *fullerenes; cocrystals; supramolecular chemistry;*

P-0774

INVESTIGATION OF THE SOL-GEL CHEMISTRY FOR THE PREPARATION OF TIO_2-ZRO_2 AND PURE TIO_2 NANOSTRUCTURED POWDERS

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Nanostructured titania materials can be used in a wide field of applications. The most popular application is maybe the use of TiO_2 nanoparticles as photocatalyst. For this application, it is important to have a look on the materials characteristics, which were found to influence the catalytic activity in a sensitive way. Desired characteristics for good catalysts are a small particle size and a large specific surface area, a high crystallinity and the anatase TiO_2 polymorph. To prepare nanostructured materials with tailored characteristics, the sol-gel process is very popular. It has been found by different research groups that the preparation of TiO_2-ZrO_2 composite nanopowders is very interesting due to the stabilization of the crystallite size and phase and an enhanced photocatalytic activity.

Different possibilities are known to influence the sol-gel chemistry and by doing so the structure of the reaction products. Nevertheless, there are to our best knowledge no systematical investigations of the influence of sol-gel chemistry on the reaction products of TiO_2-ZrO_2 composite samples, in contrast to the case of pure TiO_2 samples.

We studied the influence of the zirconia concentration on the composite powder structure and conducted further experiments concerning the influence of the chemical reaction path. The powders were prepared from titanium isopropoxide and zirconium n-propoxide precursors. Powder characterization was made with x-ray diffraction to determine the crystallite structure and size and x-ray absorption spectroscopy, which provides information about the crystallinity and the atomic environment of the absorbing species.

We found that the possibility of crystallization of the titania to anatase particles is only given for small zirconia concentrations. The crystallite size stayed nearly constant in the composite samples with increasing annealing temperature and phase transformations can substantially/successfully be suppressed, which could be derived from comparison with pure titania powders.

Keywords: *Sol-gel processes; Nanoparticles; X-ray absorption spectroscopy; X-ray diffraction;*

P-0775

SYNTHESIS AND CHARACTERIZATION OF 12-TUNGSTOPHOSPHORIC ACID IMMOBILIZED ON G-FE_2O_3@SIO_2 CORE-SHELL NANOPARTICLES AS SOLID ACID CATALYST FOR BIGINELLI REACTION

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In the field of heterogeneous catalysis, solid supported Keggin type heteropoly acids (HPAs), such as 12-tungstophosphoric acid, $H_3PW_{12}O_{40}$ (PW), arouse much attention for they not only have strong Brönsted acidity, but they can also be recovered from reaction media and reused. Among the supports that can be used to immobilize HPAs, acidic or natural substance like SiO_2, TiO_2 or active carbon are suitable and the Keggin structure of HPAs is retained upon adsorption onto their surfaces over a broad range of loading.[1] However, although these solid supported HPAs can be recovered by filtration or precipitation, lower activity or selectivity compared to homogeneous ones are commonly detected due to steric and diffusion factors. In the attempt to resolve such problems, nanomagnetically-recoverable HPA-based catalyst, was synthesized and used as novel special heterogeneous HPAs in Biginelli reaction.[2] A simple ferric oxide, γ-Fe_2O_3, was used as the magnetic material for its low price, simplicity and non-toxicity. It was coated with silica shell. After the surface coating by SiO_2, magnetic solid (designed as $\underline{\gamma\text{-}Fe_2O_3@SiO_2}$) was used as support for immobilization of PW. The obtained catalyst (designed as $\underline{\gamma\text{-}Fe_2O_3@SiO_2\text{-}PW}$) was collected by a permanent magnet and dried.[3,4] It was found that the catalyst exhibits several attractive features for the synthesis of fine chemicals.

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Keywords: *Nanoparticle; Heterogeneous catalysis; Magnetic Properties; Polyoxometalate; Supported catalyst;*

P-0776

SYNTHESIS AND CHARACTERIZATION OF $H_5COW_{12}O_{40}$ SUPPORTED ON NANO SILICA FROM RICE HUSK ASH AS A GREEN BIFUNCTIONAL NANO CATALYST

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The recent emergence of nano catalysis has received a lot of attention because it opens new perspectives for the mild catalysis of important reactions with lower environmental impact. Catalysis based on heteropoly acids (HPAs) and related compounds especially those comprising the strongest Keggin-type HPAs is an important field in which new and promising developments are being carried out both at research and technological levels[1]. Most reactions have been carried out over HPA supported on different carriers. They have excellent catalytic activity and present a greater number of surface acid sites than their bulk components[2–3]. Nano silica has been prepared from rice husk (RH), which is an agricultural waste, with high surface area and in amorphous form. Formation of reactive nano scale silica from RH is a simple process compared to other conventional techniques for its production including vapor-phase reaction, sol-gel and etc[4]. 12- Tungestocobaltic acid ($H_5CoW_{12}O_{40}$, CoW) has been supported on the silica from rice husk ash (RHA) to produce nano silica supported CoW (NCoW/SiO_2) as a bifunctional nano catalyst (as an electron transfer and strong Brönsted acid). NCoW/SiO_2 was characterized by FT-IR, XRD and TEM, also, acidic properties has been studied by potentiometric titration method. Catalytic activity of these nanocatalyst has been investigated in some organic reactions.

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Keywords: *Nanocatalyst; Heterogenous catalysis; Supported catalyst; nanoparticles; Electron transfer;*

P-0777

METAL OXIDE NANO-SHEETS WITH (111) SURFACES AS CATALYSTS AND CATALYST SUPPORTS

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The interface of the fields of catalysis and nanoscale materials is one of the most exciting areas of modern science and is at the forefront of the quest for a "green" and sustainable future. Recent progress on new methods to control the size, shape and composition of nanoscale materials and their application in renewable energy technologies are particularly intriguing. Recently, the Richards' research group has developed techniques to produce a number of new nanoscale materials that have demonstrated unique physical and chemical properties through controlled facetting. Here, recent highlights regarding these materials and their applications will be presented with a particular focus towards nanostructured metal oxides. MgO and NiO have a typical rocksalt structure and although the stoichiometry and crystallinity change little, the morphology can vary in shape, particle size and surface structure. The (100) facet of the rocksalt structure is unambiguously the most stable due to its low surface energy, therefore, it is unaminously the surface demonstrated by current wet chemical preparations. Numerous studies have demonstrated that the shape and size of crystalline MgO and NiO are highly influential on the adsorption properties. Furthermore, nanoscale MgO has been reported to be extremely effective for the destructive adsorption of numerous environmental toxins and several chemical warfare agents (VX, sarin, mustard gas). However, the (111) surface consists of alternating polar monolayers and thus, a strong electrostatic field perpendicular to the (111) surface is created. Such a surface has provided a prototype for the study of surface structure and surface reactions, which drew great attention for both experimental and theoretical studies. These studies imply the importance of size and shape control in metal oxide synthesis for their applications.

Keywords: *green chemistry; nanostructures; Heterogeneous catalysis; Supported catalysts;*

P-0778

AN EFFICIENT AND OPTIMIZED AMINOSILANIZATION OF TI6AL4V ALLOY FOR BIOMEDICAL DEVICES

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Titanium and titanium alloys are widely employed in biomedical implants due to their chemical inertia and biocompatibility.[1] The latter is generally improved by forming thin films of bioactive small molecules on the metal surface, thus preventing bacterial adhesion which represents a major concern. A common chemical functionalization of such alloys involves silanization with organosilanes such as (3-aminopropyl)triethoxysilane (APTES), thereby resulting in an aminated surface. Unfortunately, the amount of amino groups deposited and therefore available to further modification is not routinely evaluated. Moreover, there is confusion as to which reaction conditions will produce a stable and densely aminated film.[2]

In this communication we report an efficient and reproducible methodology for coating Ti6Al4V alloy with (3-aminopropyl)trimethoxysilane (APTMS). The influence of reaction time, water concentration, reaction temperature, and cross-linking conditions on surface coverage was studied. Ninhydrin assays were systematically employed to assess the density of amino groups. XPS, FTIR-ATR, and SEM analyses helped us to determine changes in both surface composition and roughness.

In addition, bacterial adhesion and biofilm formation of *Staphylococcus* ATCC35983 and *S. epidermidis* ATCC35984 were also evaluated on both silanized disks according to the above-mentioned protocol and those exposed subsequently to degradation with PBS. Adhesion and biofilm formation decreased with respect to oxidized control disks.

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Keywords: *titanium; alloys; material science; self-assembly; biological activity;*

P-0779

CHEMICAL MODIFICATION AND STRUCTURAL CHARACTERIZATION OF TI6AL4V ALLOY SURFACES

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Titanium-based medical implants are employed worldwide in bone repair. The success of this sort of regenerative medicine depends critically on appropriate chemical functionalization of the titanium surface that facilitates osseointegration, while decreasing bacterial adhesion and biofilm formation caused by quorum sensing mechanisms[1]. A common strategy involves the creation of siloxane chains attached to the metal surface and ending in halogen or amino functional groups, which further react with an organic partner that enhances the biocompatibility[2].

We report herein a robust amination of Ti6Al4V, an alloy of broad use in medical prostheses, via reaction with (3-aminopropyl)trimethoxysilane. The resulting polysiloxane network had a maximum coverage of amino groups, which underwent coupling with reactive organic molecules affording thin films on the alloy. Thus, alkyl and aryl isocyanates reacted smoothly to give the corresponding ureas. On the other hand, reaction with cinnamaldehyde gave rise to a more labile imino linkage, which can break under acidic conditions, thereby releasing this bioactive aldehyde.

Structural characterization of these chemically-modified surfaces was accomplished by FTIR-ATR, XPS, and SEM analyses. Amino group densities were monitored through ninhydrin assays. Controlled liberation of cinnamaldehyde was also checked by UV-Vis spectrophotometry and results were compared with those obtained via XPS. Studies aimed at evaluating cell proliferation as well as resistance to bacterial adhesion and growth are currently under way.

Acknowledgments. *This work was supported by grants from the Ministry of Science and Innovation (MAT2009-14695-C04-01 and CTQ2010-18938), Gobierno de Extremadura (Ayudas a Grupos Consolidados: GR10049 and GR10149) and FEDER (Fondo Europeo de Desarrollo Regional, Una Manera de Hacer Europa). One of us (ARC) thanks the Ministry for a scholarship (BES-2010-033417).*

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Keywords: *surface chemistry; material science; titanium; alloys; self-assembly;*

P-0780

PORPHYRIN BINDING AND SELF-AGGREGATION MEDIATED BY A POLYELECTROLYTE MATRIX

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Non-covalent self-assembly is an ubiquitous process in biology and it represents an effective tool in order to access to a large variety of structures with sizes spanning from nano- to mesoscopic scale showing different architectures and functionalities. Supramolecular species containing porphyrins are interesting from a fundamental viewpoint as they offer the possibility of mimicking photosynthetic centers and of accessing to supramolecular devices. In this respect, charged biopolymers, e.g. DNA, RNA, polypeptides and even filamentous bacteriophages[1] have been exploited to organize oppositely charged porphyrins in tailored assemblies. In this framework, the employment of simple polyelectrolyte templates allows to reduce the number of interaction modes of the porphyrin on the scaffold so affording **i**) to a larger stability in the formation of porphyrin aggregates in solution, as well as in the solid state and **ii**) to a better assessing of the interaction mechanism between the polymer scaffold and the chromophores.[2] Poly(sodium vinylsulfonate) (PVS), completely dissociated from its gegen ion in aqueous solution, represents an efficient and versatile highly charged polyanion template for binding various cationic species exclusively through Electrostatic Self-Assembly. Here we report on the interaction of this polymer with the tetracationic water soluble meso-tetrakis(N-methylpyridinium-4-yl)porphine (TMpyP) and some its metal derivatives (Cu(II), Zn(II), Mn(III), Au(III)) under different experimental conditions. We present evidence that, depending on pH, the high electrostatic field of PVS stabilizes the diprotonated form of the free base porphyrin at unusual pH values and causes the formation of H-type aggregates.

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Keywords: *porphyrin; aggregation; supramolecular chemistry; polyelectrolyte; spectroscopic investigation;*

P-0781

INTEGRATED 3D-PRINTED REACTIONWARE FOR CHEMICAL SYNTHESIS AND ANALYSIS

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3D-printing has the potential to transform science and technology creating bespoke, low-cost appliances which have previously required dedicated facilities. An attractive but unexplored application is using the 3D-printer to initiate chemical reactions by printing the reagents directly into the 3D-reactionware matrix, putting reactionware design, construction and operation under digital control. In this contribution, we desecribe how by using a low-cost 3D-printer and open-source design software, we produced reactionware for organic and inorganic synthesis, including printed-in catalysts, and other architectures with printed-in components for electrochemical and spectroscopic analysis. This allowed reactions to be monitored in situ so that different reactionware architectures could be screened for their efficacy for a given process, giving a digital feed-back mechanism for device optimisation. Furthermore, by solely modifying reactionware architecture, reaction outcomes could be drastically altered. Taken together, this approach constitutes a cheap, automated and reconfigurable chemical discovery platform that makes techniques from chemical engineering accessible to typical synthetic laboratories.[1] It is even conceivable that this approach could be used to undertake complex reactions and allow the reliable access to chemistry beyond the laboratory created in the 'reactionware' environment and the prospects for this will be discussed.

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Keywords: *Inorganic Chemistry; Multicomponent reactions; Polymers;*

P-0782

EFFECT OF THE AL_2O_3 AND BAO ADDITION ON THE THERMAL AND PHYSICAL PROPERTIES OF TERNARY GLASS SYSTEM

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In borate glasses, the main structural units are the [BO_3] triangles and [BO_4] tetradral which form different superstructural units like; boroxol rings, metaborate rings and chains, pentaborate, diborate, triborate and pyroborate. In this work, the Barium aluminoborate glasses were prepared. Some of properties were investigated by measure like density and chemical durability and the other by calculs. The dilatometric curves were determined and they revealed that the temperature of transition (Tg) and softening (Ts) and the dilatation coefficient increase by addition of Al_2O_3 and BaO content.

Keywords: *Barium aluminoborate glass; dilatometric curves; chemical durability; densiy; dilatation coefficient;*

P-0783

DRUG RELEASE BEHAVIOR AND ANTITUMOR EFFICIENCY OF 5-ASA LOADED CHITOSAN-LAYERED SILICATE NANOCOMPOSITES

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5-Amino salicylic acid (5-ASA) loaded chitosan-montmorillonite nanocomposites were prepared by different methods and using different ratios of modified chitosan. Chitosan (CS) was modified first through chloroacetylation followed by formation of phosphonium salt. The intercalation occurred through ion exchange process between sodium cations in MMT and phosphonium ions in the modified chitosan. The structure of the resulting composites as determined by Infra red spectroscopy (IR), X-ray diffraction (XRD), consisted of the insertions of modified chitosan between lamellar layers. The modified chitosan is strongly fixed to layered silicate. The morphology of these materials was examined by transmission electron microscopy (TEM (. The thermal stability of the nanocomposite was investigated by thermogravimetry analysis (TGA). The release of 5-ASA behavior from nanocomposites at different pH (5.4 and 7.8) was assessed and compared with the release from sodium montmorillonite (Na-MMT) and CS. The dispersed layered silicate platelets encase the 5-ASA retarding the diffusion of the drug molecule in the nanocomposite. Furthermore, their use as antitumor agents for treatment of colon cancer is investigated.

Keywords: *5-amino salicylic acid; Chitosan; nanocomposite; antitumor;*

P-0784

CONFIGURABLE REACTOR ARCHITECTURES FOR THE DYNAMIC CONTROL OF THE SELF-ASSEMBLY OF NANOSTRUCTURED MATERIALS

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Self-assembly processes are increasingly gaining importance in bottom-up synthesis of advanced materials (metal nanoparticles, quantum dots, polyoxometalates, etc.), medicine (drug release), catalysis, etc. The difficulty to control and scale-up these processes limits potential industrial applications. Herein, we present a novel set of approaches aiming to bridge this gap. Two examples are selected, which show the potential of flow systems to synthesise nanostructured materials in a highly controlled and reproducible fashion. In both cases, a set of computer controlled pumps were programmed to obtain different flow configurations to produce nanoparticles and nanostructured molecules.

The first set-up was designed to synthesise Au nanoparticles employing a continuous-flow reactor, non-conventional dielectric heating and two in-line characterisation techniques. Fine control over the properties of the nanoparticles was achieved by tuning the composition, flow rate and temperature of the reactor. A second configurable reaction system was employed to dynamically control the self-assembly of nanoscale polyoxometalates. The control was achieved by simultaneously tuning a single parameter in three interconnected reactors. This represents a revolution in flow based complex chemical discovery.

Keywords: *self-assembly; nanoparticles; flow; gold; polyoxometalates;*

P-0785

THIN FILM HETEROJUNCTIONS BY CARBON NANOTUBE DERIVATIVES WITH ENHANCED SOLUBILITY AND OPTICAL PROPERTIES

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The combination of single-walled carbon nanotubes (SWNTs), characterized by high electron mobility, with p-type semiconducting polymers could lead to an overall improvement in the exciton dissociation and carrier extraction efficiencies in practical devices.[1] However, one of the main concern in the use of SWNTs, relates to the their scarce solubility. Chemical modification has been widely employed to increase the solubility of SWNTs, but usual reaction conditions limit such syntheses to a small scale with low productivity.

Here, we employ SWNTs which have been functionalized with aromatic and heteroaromatic moieties via 1,3-dipolar cycloaddition and through diazotization reaction under batch and continuous-flow conditions. This offers a safer, scalable processing and the opportunity to a rapid reaction screening using a relatively small amount of reagents.[2]

Such systems in combination with P3HT have been used to fabricate bulk heterojunctions (BHJ) by Langmuir-Blodgett, which offers a simple method of producing ultrathin-films with fine control over thickness. Thanks to the improved solubility of SWNT derivatives we prepared multi-planar heterojunctions (MHJ) consisting of alternate layers of P3HT and SWCNTs, by horizontal lifting (Langmuir-Schaefer) technique. Then we induced a transition from MHJ to BHJ by thermal annealing to mix the layers.

While the degree of functionalization ensured by diazotization, higher than 1,3-dipolar cycloaddition, improves processability, fluorescence quenching measurements have demonstrated that thienyl groups ensure a stronger interaction with P3HT and consequently a better electron transfer. Such properties have been modulated within the thin film by changing its internal morphology tuning the parameters of the mixing process. Thienyl derivatives obtained through controllable functionalization of SWNTs in flow conditions are promising candidates for the incorporation in the active layer of OPV cells.

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Keywords: *Nanotubes; Langmuir-Blodgett films; Electron transfer; Thin films; Energy conversion;*

P-0786

INFLUENCE OF OXYGEN PARTIAL PRESSURE ON THE GROWTH AND PHOTOCATALYTIC ACTIVITY OF WO_3 FILMS PREPARED BY MAGNETRON SPUTTERING

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Several semiconductor materials have been reported to offer high photocatalytic activity to degrade organic and inorganic pollutants. Among them TiO_2, has been employed extensively as photocatalyst, however the drawback is the wide band gap (3.2 eV) limiting its use to the UV part of electromagnetic spectrum (2–3%) under sunlight. WO_3 is also an important photoactive material with a band gap energy of 2.5 eV and can absorb the blue part of solar spectrum up to ca. 500 nm.

In this work, WO_3 films were deposited on unheated glass and conductor glass substrates by DC reactive magnetron sputtering using a tungsten target. The depositions were carried out in a mixture of Ar and O_2, at constant total sputtering gas pressure (P_T) of 0.8 and 1.6 Pa and sputtering power of 220 W. The oxygen partial pressure (PO_2) was changed between 10 and 100% of P_T. The as-sputtered films were thermal annealed in air atmosphere at 400 ºC for 2 h. The films were characterized by X-ray diffraction, scanning electron microscope, atomic force microscopy and UV–Vis spectroscopy.

It has been revealed that the PO_2 is a key factor on the structural, morphological and optical properties of WO_3 films as observed in similar study with TiO_2 films[1].

The films photocatalytic activity was tested, under visible irradiation, on the decolorization of Rhodamine 6G aqueous solutions. The dye photodecolorization process was studied considering the influence of the crystallinity and preferred orientation of growth of the prepared films.

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Keywords: *Thin films; Nanotechnology; Heterogeneous catalysis; Surface analysis; UV-Vis spectroscopy;*

P-0787

BISMUTH NANOPARTICLES FOR THERMOELECTRIC MATERIALS GENERATED BY LASER ABLATION OF BISMUTH OXIDE SUSPENDED IN ORGANIC LIQUIDS

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The ongoing search for sustainable sources of electric energy leads to great efforts to improve the efficiency of thermoelectric generators (TEG). The efficiency of TEG can be described by the figure of merit $zT=(\sigma\ S\ T)\ /\ (\kappa_{el}+\kappa_{ph})$ with σ - electrical conductivity, S - Seebeck coefficient, T - temperature, κ_{el} - thermal conductivity caused by electrons and κ_{ph} - thermal conductivity caused by phonons.

One attempt to get higher zT values is to decrease the thermal conductivity caused by phonons while keeping the other parameters nearly constant.[1] This is possible through phonon scattering at specific introduced grain boundaries. Thus nanostructured materials like nanoparticles can be used to improve the efficiency of TEG.

We focus on the synthesis of bismuth based nanostructured materials by laser ablation. Laser ablation of solid targets is a well know method to get colloidal solutions of metal nanoparticles.[2] Unfortunately the production rates are relatively low. This drawback can be overcome by the usage of the corresponding metal oxide powder instead of the bulk metal targets.[3] We report the formation of bismuth nanoparticles by laser ablation of Bi_2O_3 powder suspended in organic solvents. This approach will be extended to bismuth based semiconductors like Bi_2Te_3.

The obtainted nanoparticles are characterized by atomic force microscopy and transmission electron microscopy.

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Keywords: *bismuth nanoparticles; laser ablation; transmission electron microscopy; thermoelectric materials;*

P-0788

THE ELECTROCATALYTIC ACTIVITY OF NANOSTRUCTURED NI-COATED SCREEN-PRINTED CARBON ELECTRODES

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The mass fabrication of useful thick film-electrodes is achieved by screen-printing technology, which is known as a simple and fast method. Its ability to produce inexpensive and reproducible substrate electrodes is one of their most attractive characteristics and designates screen-printed electrodes for further modifications. Screen-printed effective electrochemical sensors, in particular, those for the detection of glucose, hydrogen peroxide, cholesterol and phenolic compounds, are commercially avalaible. The way of performing routine electroanalysis has been revolutionized by these sensors and can be viewed as disposable single-use sensors onto which a droplet of the sample is directly deposited. It has been reliably accomplished that screen-printed electrodes can be certainly prepared and applied for the determination of a great variety of biomolecules and several inorganic species. In an effort to improve the performance of the screen-printed electrodes (SPEs), in terms of sensitivity and specificity, several bulk or surface modification routes have been adopted. Enzyme-modified SPEs are highly applicable in environmental analysis, while other SPEs are useful as immunosensors, or in genetic and drug testing [1, 2]. We present here screen-printed carbon-based electrodes (SPCEs), coated with Ni film as a novel alternative to the unmodified electrodes. In an effort to achieve reproducible film-modified SPCEs we used electrochemical deposition as a convenient and fast method for the preparation of Ni-SPCEs. In this way, these disposable substrate electrodes acquire very specific electrocatalytical properties even being re-useable. The morphology and homogeneity of nano-scaled surface Ni-modified SPCEs was studied by scanning electron microscopy. The electrocatalytical activity of Ni-coated SPCEs was evaluated by hydrogen evolution reaction (HER) opening the way to rapid 'in-situ' analyses.

Acknowledgement: *The authors wish to thank M· SR VEGA 1/0211/12 for financial support.*

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Keywords: *Immunoassays; Nanoparticles; Nickel; Proteins; Sensors;*

P-0789

PREPARATION AND CHARACTERIZATION OF DRUG LOADED CHITOSAN NANOPARTICLES

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The aim of the present study was to prepare drug loaded chitosan nanoparticles (NP) using trastuzumab as homing device. Trastuzumab is a monoclonal antibody directed against extracellular domain of the human HER-2 receptor, over expressed in non-small cell lung carcinomas. As HER-2 receptor is accessible on the cell surface, trastuzumab provides a promising target to cancer cells thus achieving cell type specific drug carrier system.

Chitosan NP's were obtained by inducing ionic gelation with TPP. The blank NP's were loaded kinase inhibitor drugs. NP's were concentrated by centrifugation and lyophilized. The supernatant was collected for unbound drug analysis.

The antibody was thiolated and added thiol groups was quantified by Ellman's test. The chitosan NP's was decorated with thiolated trastuzumab by a linker. The antibody-NP binding efficiency was determined by using ITC. HER-2 expression in lung cancer cell lines was performed using western blotting and flow cytometer. *in vitro* cell specific binding efficiency of the trastuzumab decorated NP's will be determined for the lung cancer cell lines.

The formation of chitosan NP is dependent upon on the gelation procedure, which is controlled by the addition of TPP. The mean particle size for the lyophilized chitosan NP's from DLS ranged from 60.66 ± 0.2, 84.81 ± 0.4 and 107.56 ± 5.0. The mass spectrometry data indicated 80% encapsulation of the drug with the chitosan NP's.

Thiolation of trastuzumab with 2-iminothiolane introduces additional thiol groups. The number of sulfhydryl groups introduced per trastuzumab was 0.91 ± 0.15. It is expected that chitosan NP's decorated with trastuzumab will be produced and characterized. It is also expected that trastuzumab decorated NP's will have enhanced cell penetration in comparison to the non-decorated NP's using cancer cells. We also expect superior cytotoxic effect by the decorated NP's when compared to the non-decorated chitosan and unprocessed drug.

Keywords: *analytical method; Mass Spectrometry; Nanoparticles;*

P-0790

THE PREPARATION AND ANTIBACTERIAL ACTIVITY OF POLYMER-STABILIZED SILVER BROMIDE AND SILVER NANOPARTICLES

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The thesis presents the preparationof silver bromide nanoparticles and their subsequent reduction to metallicnanoparticles by the using of sodium borohydride as reducing agent. Thisproposed method using consecutive reactions enable efficient comparing ofproperties of silver bromide and silver nanoparticles. Clear colloiddispersions of silver nanoparticles and primarily of silver bromidenanoparticle are aggregately unstable and because of that, there were usedseveral polymers as stabilizers. The chosen polymers were also used as particlesize modifiers and their using enabled the preparation of silver bromide andsilver nanoparticles with the different sizes ranges between 55 and 112 nm forAgBr and between 39 and 93 for Ag nanoparticles. Prepared dispersions of silverbromide and silver nanoparticles were tested for their antibacterial andantifungal activity. This was tested against several types of gram-positive andgram-negative bacteria and against several strains of candida. Finally,obtained results of biological activity of prepared silver bromide and silvercolloidal dispersions in the presence of various polymers were compared witheach other.

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Keywords: *silver; nanoparticles; reduction; Biological activity;*

P-0791

ORGANIC SELF-ASSEMBLED MONOLAYERS AS A TOOL FOR LOW TEMPERATURE WAFER BONDING

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Silicon photonics is an important research field because of the promise of large scale integration of electro-optic devices alongside electronics. A potential approach to *active* silicon-photonic devices relies on the vertical integration of electro-optic materials, such as germanium or III-V semiconductors, alongside silicon for the making of hybrid devices. Such devices support propagating modes that overlap both materials, and bring together the guiding of light in silicon and its manipulation in other electro-optic materials.

Hybrid devices that rely on wafer bonding processes between dissimilar materials pose numerous challenges. The direct bonding approach is typically a high temperature process. An alternative process uses a polymeric glue and typically results in a relatively thick (tens of nm or more) inter-phase.

We report herein an alternative paradigm for the bonding of various electro-optic materials to silicon. The bonding procedure relies on the deposition of an organic self-assembled monolayer on the surface of one or both wafers, and their subsequent bonding through controlled surface chemistry between the monolayers on the surfaces of the wafers, or between one monolayer and the surface of the other wafer itself. Using variously functionalized monolayers, we report the bonding of two silicon wafers, as well as the bonding of silicon to optical materials such as InP and $LiNbO_3$. All processes were carried out at temperatures £ 150 °C and the bonding interface has a thickness of only a few nm. We have also directly interrogated the integrity of the bonding interface and developed methodology for measuring the strength of the bond between the two substrates.

The monolayer-based approach to wafer bonding should enhance the strength and yield of such device fabrication processes. It should reduce the thermal stresses and out-gassing often associated with current bonding approaches and should broaden the range of materials that can be bonded.

Keywords: *self-assembly; monolayers; surface chemistry;*

P-0792

HOMOCHIRAL METAL-ORGANIC FRAMEWORK CRYSTALS FOR ASYMMETRIC CATALYSIS AND ENANTIOMER SEPARATION

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The field of metal-organic frameworks (MOFs) has grown explosively in recent years and numerous studies have been reported owing to their potential applications in gas storage, separation and heterogeneous catalysis. While a large numbers of MOF are being discovered so far, only a few examples of chiral MOF for enantioselective separations or heterogeneous asymmetric catalysis have been investigated. Here, we wish to report the synthesis of a novel chiral porous metal-organic framework (*R*)-MOF and its function as asymmetric heterogeneous catalyst for the alcoholytic kinetic resolution of styrene oxide during ring opening reaction to 2-methoxy-2-phenylethanol. Chromatographic enantiomer separations of some sulfoxides over a chiral metal-organic framework in HPLC are also reported.

Keywords: *Asymmetric catalysis; Metal-organic frameworks; Kinetic resolution; Heterogeneous catalysis; Supramolecular chemistry;*

P-0793

SYNTHESIS OF NEW AZO COMPOUNDS IN ORDER TO VARY SURFACE PROPERTIES

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The immobilization of π-conjugated systems with electro-optical properties on gold surfaces by formation of self-assembled monolayers (SAMs) is a focus of high interest.[1] Reversible photoswitching devices were demonstrated with azobenzene and diarylethene derivatives and open the route for potential applications as optical switches in molecuar electronics, molecular machines, photoswitchable surface wettability, and biosensors.[2] Molecular rods incorporating azo units and organized in SAMs, undergo efficient photoisomerization producing cooperative molecular movements able to express mechanical work.[3, 4] The potential for manipulation and control inherent in molecule-based motors holds great scientific and technological promise.

For this purpose, we have designed and prepared new rigid, rod-like azobenzenes comprising a terminal sulfur anchor group. These compounds might harness the force expressed by azo SAMs, in order to move vertically nano-particles sitting on the azo SAMs, and move laterally nano-particle, by sweeping across the surface patterns formed by alternating *Z*- and *E*- isomers. We have also developed syntheses of previously unknown azobenzenes carrying long brush-like hydrophilic resp. fluorophilic chains, which should display large differences in hydrophilicity resp. fluorophilicity between *E*- and *Z*- form upon immobilization on a surface. The synthetic methodology described here provides versatile synthetic pathways to azobenzene derivatives that might be used as potential photo-responsive nanoscale devices.

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P-0794

DESIGN AND SYNTHESIS OF SWITCHABLE MOLECULAR TWEEZERS

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Molecular recognition of substrates is an important challenge in supramolecular chemistry. Among host-guest molecular systems, molecular tweezers[1] have generated increasing interest during the past few years especially for the recognition of small organic molecules. At the frontier of dynamic supramolecular systems, the development of switchable molecular tweezers[2] has opened up a wide field of applications in molecular transport by complexation-release, drug delivery, magnetic or luminescent switches.

We are interested in the design of molecular tweezers switchable by coordination[3] for reversible molecular recognition. Our system is based on a terpyridine ligand substituted in 6 and 6'' positions by two arms bearing molecular recognition moieties. The terpyridine unit can switch upon metal coordination between a "W" shaped open form and a "U" shaped closed form bringing the two recognition units in an optimal geometry for recognition of flat aromatic substrates. Upon decoordination the tweezers will reopen releasing the intercalated substrate. The recognitions units are based on salen complexes with magnetic or luminescent properties depending on the metallic center for sensing.

The design and synthesis of a terpyridine(Ni-salen)2 based molecular tweezers will be presented as well as its reversible switching and molecular recognitions properties.

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Keywords: *Molecular tweezers; Molecular switch; Supramolecular chemistry;*

P-0795

NANOPARTICLES IN TWO-PHASE SEPARATION METHODS

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One of the most important ways to raise the degree of purity of substances is to improve the methods of high purification for new type of impurities. These new impurities are impurities in the form of suspended particles of submicron size and recently named nanoparticles [V.M. Vorotynsev Nanoparticles in two-phase systems.- Moscow: Izvestiy.2010.-320 p].

The peculiarity of the current stage of technology development of high-purity substances is a merging of the size of a number of heterogeneous impurities with impurities in molecular form. Behavior of nanoscaled particles in the two-phase distillation and crystallization methods of separation requires new conceptual apparatus and new technological approaches.

In this report are considered the concepts of nanoparticles as impurities in high-purity substances, the nature and method of its generation in gas, liquid and solid substances. Investigation of high purification of liquids from suspended nanoparticles including experimental determination of separation coefficient of nanoparticles between liquid and vapor, method for determining the content of nanoparticles, determination of its separation coefficient, dependence of nanoparticles separation on their size and the velocity of distillation. Also it is considered the high purification from nanoparticles by rectification. It was given the design of apparatus for new separation method – termodisstillation. It was shown the application of termoditillation method in silicon and germanium production, in epitaxial structures production and in optical fiber raw material production. It was considered the distribution of nanoparticles in the phase equilibrium in the crystallization process. The mechanism of capture of nanoparticles from melt by the growth crystal has been proposed. It was shown the transition of nanoparticles from melt to crystalduring the crystallization for electrolyte and nonelectrolite solutionsIt is considered the dependence of separation factor countercurrent crystallization column on the fraction of recrystallized solid phase and dependence of separation factor.

Keywords: *nanoparticles; distillation; crystallization; high-purity substances; silicon;*

P-0796

FABRICATION OF GOLD MICRO-STRUCTURES VIA REACTION BETWEEN HYDROXYLAMINE AND CHLOROAURIC ACID

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Reaction between chloroauric acid ($HAuCl_4$) and hydroxylamine hydrochloride ($NH_2OH{\cdot}HCl$) is widely used in a seed-mediated growth of gold nanoparticles. It is commonly believed that hydroxylamine can reduce Au^{3+} ions to Au^0 only in the presence of metallic gold. The possibility of nucleation in the mixture of $HAuCl_4$ and $NH_2OH{\cdot}HCl$ has never been confirmed experimentally and, until now, has been remaining only a hypothesis.

Here, for the first time, we demonstrate the evidence of nucleation in mixtures containing aqueous solutions of chloroauric acid and hydroxylamine. Moreover, we employ this reaction as a powerful tool in a fabrication of new metallic nano-materials.

In our approach, gold micro-flowers (AuMFs)—metallic particles of expanded nano-structured surface—are formed in the bulk solution. In the process the AuMFs sediment and deposit onto solid substrate. The method offers easy control both over the AuMFs morphology and density of the gold coating, which is formed as a result of the deposition of the AuMFs. Also, by addition of halides or silver ions to the reaction mixture we can to a great extent modify the morphology of the resulting coating. In particular, for certain compositions of the reaction mixture, a porous metallic film can be obtained instead of the micro-flower coating. Both the thickness and the roughness of such films are controllable by the mixture composition.

The metallic layers obtained with our method have been used as efficient platforms for chemical and biological sensing based on surface enhanced Raman spectroscopy (SERS). The obtained platforms have been proven to be mechanically stable and to have good SERS enhancement factors as well as excellent repeatability.

Keywords: *nanostructures; microporous materials; surface plasmon resonance;*

P-0797

THE SYNTHESIS OF NOVEL NANOPARTICLES IN SUPERFLUID HELIUM NANODROPLETS

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Helium nanodroplets are large helium clusters typically containing 10^3-10^6 helium atoms.[1] They are superfluid and have an exceptionally high thermal conductivity; as a result, foreign species, when captured by helium nanodroplets, can be cooled rapidly to the equilibrium temperature of helium nanodroplets, 0.38 K, by evaporative loss of helium atoms.[2] Most atoms and all molecules enter helium nanodroplets rather than sit on the surface; when more than one dopant is picked up, agglomeration of dopants will occur. Consequently, the potential exists for growing not only small atomic and molecular clusters, but also much larger objects such as nanoparticles, inside helium nanodroplets. This capability has been demonstrated, for the first time, in Dr Yang's research group at the University of Leicester, where core-shell molecular clusters with small water clusters as the core were synthesised.[3]

In this presentation, we will briefly overview the fundamentals of helium nanodroplets as uniquely powerful but astonishingly versatile nano-reactors for synthesising nanoparticles, as well as new experimental results on core-shell structures and metal nanoparticles that have been obtained by Dr Yang's research group at the University of Leicester.

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Keywords: *Helium nanodroplets; core-shell nanoparticles;*

P-0798

SYNTHESIS OF A DENSELY PACKED CYLINDRICAL DENDRONIZED POLYMER OF GENERATION 6

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Dendronized polymers (DP) are a class of comb polymers to which a regularly branched unit (dendron) is attached to each repeat unit.[1] In recent years a divergent methodology has been developed by which a series of DP was synthesized up to the 5th generation (**PG5**), which is the largest synthetic linear macromolecule.[2] The structure perfection for each generation was quantified by a UV labeling method.[3] The resulting DP show generation dependency in their thickness, persistence length and stretching elasticity.[1,4]

Higher generations (≥6) are also of particular interest, because theoretical studies suggest that the 6th generation DP (**PG6**) is close to the highest possible generation (g_{max}, which is 6.1) that can accommodate all perfect dendrons.[5] At or above g_{max} all the atoms in the dendritic architecture will be packed densely with no "unused space" that would allow conformational change. These DP will be "molecular objects", which do not change their cross-sectional size and shape irrespective of their environments.[6]

Here we report the synthesis and characterization of the first homologous DP series that includes **PG6**, which is a densely packed organic cylinder. Its properties are currently being explored.

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P-0799

PHOTOTHERMAL CONVERSION OF GOLD NANOPARTICULES PROBED BY LOCAL POLYMERIZATION

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Metallic nanoparticles have been playing a very important role in the development and applications of nanotechnology. For example iron, cobalt, and nickel magnetic nano-particles are used as contrast agents in magnetic resonance imaging. Silver nanoparticles are known to have antibacterial function and can be used in bio-physics and bio-medical applications.

Optical properties of metallic nanoparticles are mainly dominated by the Localized Surface Plasmon Resonance (LSPR) at optical frequencies. At this specific frequency, nano-particles exhibit intense absorption and light scattering due to the LSPR. Moreover, metal nanoparticles are able to transform absorbed light into heat. This photothermal conversion effect has been used for many applications. In particular, it has been used in the development of photothermal therapies (hyperthermia) for cancer treatment, as well as laser ablation as a technique of malignant cell destruction. More recently, plasmonic heating has been used to promote drug release through polymer phase change, hybrid DNA cleavage, or enhanced diffusion.

We propose here a new approach based on nanopolymerization thermally initiated to characterize the heat pattern in the vicinity of photoexcited gold nanoparticles (GNPs). For this we developed thermopolymerizable formulations that are characterized by a controlled threshold temperature (Tth) of polymerization. Below this threshold temperature, the polymerization cannot occur. This sharp control allows us to use such material as thermal nanoprobe to measure the local temperature around the particle as well as to print the heat distribution around the nanoparticule.

Keywords: *Nanotechnologie; Nanoparticles; Polymerization; Gold; polymers;*

P-0800

DENDRONIZED POLYMERS: ORGANIC NANOCYLINDERS WITH TUNABLE THICKNESS

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Dendronized polymers (DP) are a class of polymers, which carry dendrons on each backbone repeat unit.[1] By grafting dendritic groups from a polymer backbone in a divergent fashion, a series of cylindrical polymers with tunable thickness (~1-10 nm) has been synthesized with high precision (>97% structure integrity) and efficiency (addition of 1×10^8 Da in one step). This powerful method using simple organic chemistry allows organic synthesis to enter the dimention of biology: at the 5th generation level the largest synthetic linear macromolecule was produced and compared with Tobacco Mosaic Virus.[2]

Can the nano-construction go further? According to the theoretical predictions, the maximal generation (g_{max}), beyond which perfect dendritic structures cannot be obtained, is ~6.1.[3] However, the imperfect polymers above g_{max} can still be prepared and will be densely packed cylindrical organic objects, with no "unused" internal space to mediate responsivity. DP of the 6th generation (**PG6**), which is the last generation below g_{max}, has been recently synthesized and characterized in our laboratory. Being close to g_{max}, **PG6** outstands among the homologous series, regarding the structure perfection, atomic mobility and deformability. This offers for the first time the chance of a true cylindrical "molecular object".[4]

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Keywords: *synthesis; shape persistence; dendrimers; dendronized polymers; molecular objects;*

P-1014

POROSITY OF ROBOT LASER HARDENING SPECIMENS

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Porouse structure in material is one of important mechanical property which impact on hardness of materials. We study was limited on tool steel standard label DIN standard 1.7225. We can not apply Evclidian geometry to describe porouse of hardened specimens, thus we use very good method, fractal geometry. The specimen test section had a cylindrical form dimension 25×10mm (diameter×high). Speciment with the porosity about 19% to 50%, were prepared by laser technic, followed by hardening at T? [800, 2000] °C and v?[2,5] mm/s. Also, we changed one parameter of robot laser cell, temperature T ? [1000, 1400] °C to 50 °C steps. Microstructure of specimens was observed with an field emission scanning electron microscope JSM-7600F JEOL company.

To investigate the possibility of application of fractal analysis to heat-treated surface, we have examined the relation between surface porosity and fractal dimensions depending on various parameter of temperature of robot laser cell. Also we present temperature of robot laser cell impact on poruse specimens in process of robot laser hardening. We are interested to calculate relationship between fractal dimension and porosity in:

- two-beam laser robot hardening (laser beam is divided into two parts),
- areas of overlap (the laser beam covers the already hardened area),
- robot laser hardening at different angles (the angles change depending on x and y axis).

P-0801

GOLD-CATALYZED CYCLOISOMERIZATION REACTIONS OF VINYLALLENE DERIVATIVERS

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Allenes are present in many natural products and biologically active compounds. Over the years the use of catalytic reagents for the synthesis of allenes has highly developed. Several useful methods for synthesis of vinylallene derivatives have also been reported.Recently, vinylallenes were found to undergo gold-catalyzed cycloisomerization reaction to give cyclopentadiene derivatives.In this study, vinylallene derivatives which bear electron-donating or -withdrawing groups on the aryl moiety were subjected to the gold-catalyzed cycloisomerization reaction to examine the effect of the substituents on aryl moiety. Their gold-catalyzed cycloisomerization reactions afforded the formation of cyclopentadiene derivatives in high yields via C-C bond formation. Surprisingly, we found that an aryl shift took place to the central carbon atom of the allenic moiety. Moreover, the reaction was highly depending on the substituents at the aryl, allenyl, and alkenyl group.

Keywords: *vinylallene; gold; cycloisomerization;*

P-0802

SILICON TETRACHLORIDE MEDIATED ORGANOCATALYTIC ALDOL REACTION

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Aldol addition reaction is one of the important and most studied carbon-carbon bond forming reactions in organic chemistry. The idea behind the catalysis of Aldol reactions emerged from the similarity between allylsilane addition and silyl enolether addition (C-Si bond cleavage and O-Si bond cleavage). In catalytic asymmetric aldol addition reactions, new stereogenic centers with controllable absolute configurations are formed which is also important in synthesis of natural products.

Different from the Mukaiyama-type aldol reactions, recently, chiral lewis bases have been used as promoters and in the presence of $SiCl_4$, these reactions proceed through the formation of a cyclic transition state leading to anti aldol product as a major product with moderate-to-good diastereoselectivities and enantioselectivities. Phosphoramide derivatives, BINAPO and its derivatives, and N,N-dioxides and N-oxides have been extensively used for this purpose.

Recently, our group has designed new phosphineoxy aziridinyl phosphanates (POAP) as organocatalysts which can be synthesized easily starting from vinyl phosphonate by Gabriel-Cromwell reaction. These organocatalysts were used for the asymmetric aldol addition reaction. Cyclohexanone and different aldehydes were reacted in the presence of $SiCl_4$ and POAP organocatalyst to form aldol product. Although the optimization studies are still continuing, the results so far showed that aldol product can be obtained in good yield and reasonable enantioselectivity. At this conference the synthesis of POAP organocatalyst and the details of organocatalytic aldol reaction will be presented.

Keywords: *Asymmetric synthesis; Aldol reaction; Organocatalysis; Silicon- based;*

P-0803

PREPARATION AND STUDY OF LIQUID CRYSTALLINE BEHAVIOUR AND ELECTRICAL PROPERTIES OF A DIFFERENT TYPES OF SCHIFF'S BASES DIMMERS AND IT IS COMPLEXES

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Preparation of three different series of the symmetrical twin dimmers (Schiff's bases) are derived from benzidine. Besides, Preparation and study of the liquid crystalline behaviour was achieved for eight compounds of (I) series.

These prepared compounds characterized by I.R, UV-spectroscopy, and 1HNMR technique. The liquid crystalline properties of this prepared compounds was verified by optical polarizing microscopy and differential scanning calorimeter (DSC) and thermal gravimetry analysis (TG). The mesomorhic behaviour of these compounds was found to be nematic (enantiotropic), while three compounds (Di-9-anthrylidene benzidine, Di-4-hydroxy benzylidene benzidine, and Di-3-methoxy-4-hydroxy benzylidene benzidine) did not show any liquid crystalline behaviour. It has been found the nematic range exhibited by these compounds follows the order:

$$MeO > NO_2 > H > Cl$$

In addition, preparation and characterization were achieved for four complexes of Schiff's bases with ions of (Cu^{+2}, Ni^{+2}): (DMeOBB-Cu^{+2}, DMeOBB-Ni^{+2}, NO2BB-Cu^{+2}, NO2BB-Ni^{+2}) were found to be nematic (enantiotropic). It is found that the (D.C) electrical conductivity ranged from (10^{-12}) to (10^{-9}) (ohm. cm)$^{-1}$ lies in the usual range of organic semiconductors.

P-0804

SYNTHESIS AND ANTIMICROBIAL ACTIVITIES OF SOME NEW SYNTHESIZED IMIDE AND SCHIFF'S BASE DERIVATIVES

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A series of macrocyclic imide and Schiff-base derivatives **2** and **3** have been prepared from pyridine-N-amino derivatives **1** as starting material according to the literature procedures[1–4]. A series of 2,6-bis(substituted thiazolopyrimi-dinyl) pyridine **(2a, b)** and corresponding Schiff's bases **(3a-j)** were synthesized from 2,6-bis-(3-amino-2-methyl-4-oxo-9-substituted-3,4-dihydropyrido--[30,20:4,5]-thieno[3,2-d]pyrimidin-7-yl)pyridines **(1a, b)** as starting materials. The compounds **1a,b** were reacted with 2,3,4,5--tetrachlorophthalic anhydride in glacial acetic acid to give the corresponding bis-imides **(2a, b)**. But, they are treated with aromatic aldehydes in refluxing ethanol to afford the Schiff's base derivatives **(3a-j)**. The antimicrobial screening showed that many of these newly synthesized compounds had good antimicrobial activities comparable to Streptomycin and Fusidic acid as positive controls. The detailed synthesis, spectroscopic data, and antimicrobial activities of the synthesized compounds will be reported.

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Keywords: *macrocyclic imide; Schiff-base; Synthesis; Antimicrobial;*

P-0805

(6-HYDROXY-3-OXO-3H-XANTHEN-9-YL)METHYL: A PHOTOREMOVABLE PROTECTING GROUP ABSORBING ABOVE 500 NM

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Photoremovable protecting groups (PPGs) are a versatile synthetic tool which found many applications in caging of biomolecules.[1] Coumarin-based PPGs have strong absorption extended to the visible light and fast release rate from its excited singlet state, and they gained considerable attention, especially for their applications in biological chemistry[2] and caging of cyclic nucleotides, carboxylic acids, and phosphates.[3-6] To extend the wavelength range of coumarin PPGs, we synthesized and studied a structurally similar (6-hydroxy-3-oxo-3*H*-xanthen-9--yl)methyl derivatives with three different leaving groups ($OP(=O)OEt_2$, OAc, and Br) in 7 steps with an overall chemical yields of 20–25%. The formation of a CT complex of **1a-c** with DDQ during synthesis was observed and investigated by comparative study with the interactions of DDQ with succinylfluorescein and its methyl ester.[7] All derivatives of release the leaving groups in aq buffer at pH = 7 upon irradiation with a 546-nm green light. The quantum yields of photorelease were found in the range of 0.5–4.2%. The MO calculations suggested that the heterolytic release of a leaving group strategically attached to the xanthenyl chromophore occurs from the first excited singlet state.[8, 9]

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Keywords: *Photoremovable protecting groups; Coumarin; CT complex; Xanthene; Chromophore;*

P-0806

PERSPECTIVES IN THE DESIGN, SYNTHESIS AND CHARACTERIZATION OF POLYMER MATERIALS WITH APPLICATIONS IN OPTICAL FIELD

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The organic macromolecules with extended electronic sequences remain one of the most attractive points of start for implementation of the specialized device. Why the polymer systems? Because is relatively easy to process organic polymeric materials into practical devices. They are certainly remarkable materials through their flexibility, versatility and architectural accessibility, which allow their optimization for the desired applications.

Since the discovery of the photorefractive effect in organic polymers, polymers containing carbazole have also attracted much attention for their photoconductivity. In this context, multicomponent polymers with structural units containing both photoconductive and electrooptic functionalities in the side chain can be regarded as potentially suitable materials for photorefractive applications. Indeed, polymers with the carbazolyl diazene side group prepared by polymerization of the corresponding functionalized monomers, or by azocoupling post-reaction to carbazole containing polymers, proved to show photorefractive and NLO properties as well as photoinduced orientation and formation of surface relief gratings. Moreover, the helical configurations, particularly the 'stacking' of the carbazole pendant groups in the syndiotactic polymer, would allow for many of the interesting electronic and photoconductive properties associated with polyvinylcarbazole. The such materials can be characterized, in solution, by chiral conformations related to the combined effects of the strongly dipolar conjugated carbazole system with the conformational stiffness of optically active rings, favouring the instauration of a conformational arrangement with a prevailing handedness, at least for chain sections of the macromolecules.

In this idea, we propose the synthesis and characterization of few new carbazole compounds, to foreshadowing, based theirs physical properties, the potential applications of polymer materials, with such sequences, in the nonlinear optical field. Structured in three sections, the aims is to highlight the most important peculiarities regarding the structural - constituent relationship to the polymer materials, based on the consacrated analytical techniques.

Keywords: *Azo compounds; polymers;*

P-0807

PROTON-CATALYZED, SILANE-FUELED INTRAMOLECULAR FRIEDEL–CRAFTS ARYL COUPLING: FLUOROARENE C–F ACTIVATION BY SILYL CATIONS

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Friedel–Crafts transformations are known for a long time and still present a very important class of chemical reactions. In terms of aryl-aryl couplings, the reaction is limited due to the thermodynamic instability of the phenyl cation. This fact gave rise to a large variety of coupling reactions using transition metal catalysts and activated arenes. Combining our group's knowledge about silylium ions in general[1] and our findings on carbon fluorine bond activation,[2] we developed a method for an intramolecular Friedel–Crafts type coupling of an aryl fluoride with an unactivated aryl nucleophile without using a transition metal.[3] The transformation involves cleavage of the C–F bond using the very reactive silylium ion and attack by an adjacent arene moiety within the same molecule. In our example reaction, we use an $i\mathrm{Pr}_3\mathrm{Si}$ carborane to abstract fluoride from 1-(2-Fluorophenyl)naphthalene, which is transformed to fluoranthene by ring closure and subsequent elimination of a proton. Since the proton can be used to generate a silyl cation from a silane, only a catalytic amount of initiator (i.e. silylium ion) can be used. We applied this method to more complex systems towards larger polyaromatic hydrocarbons and are exploring the possibilities concerning substrate scope and adaptabilities of the reaction.

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Keywords: *silyl cations; C-F activation; Friedel–Crafts; polyaromatic hydrocarbons; proton-catalyzed;*

P-0808

MANIPULATION OF THE ALPHA,BETA-UNSATURATED CARBONYL UNIT OF CHALCONES AS TOOL TO FINE-TUNE REACTIVITY AND BIOLOGICAL ACTIVITY

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Michael acceptors are often referred to as being nonspecific and have widely been neglected in drug development. *Gribble* and *Sporn* et al. showed that a variation of the α-substituent of an α,β-unsaturated carbonyl system can directly influence biological activity.[1] We are interested to use new in α-position of the α,β-unsaturated carbonyl system modified enones[2] to address specifically thiols which are of great biological importance.

To test this concept, we investigate the expression and activity of proteins such as heme oxygenase-1 (HO-1) and inducible NO-syn-thase (iNOS). These enzymes are important targets within inflammatory processes and are regulated by the transcription factors Nrf2 and NF-κB. In both regulation mechanisms sulfhydryl groups are essential for activation or inhibition, and therefore Michael acceptors could be applied.

We were able to synthesize a library of α-substituted chalcones (1,3-diphenylpropenones), X-derivatives, and test their reactivity in kinetic measurements using thiols. Here, we could clearly demonstrate that the substituent X has a great influence on the second order rate constant k_2. Moreover, we tested their influence on the activity and expression of the proteins HO-1 and iNOS.

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Keywords: *Synthesis design; Michael addition; Inflammation; Kinetics; Protein expression;*

P-0809

METAL CATALYZED ASYMMETRIC CASCADE 1,3-DIPOLAR CYCLOADDITION REACTION OF AZOMETHINE YLIDES

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In recent years cascade reactions have been studiedsignificiantly by different groups. This reaction provides complex moleculesfrom very simple starting materials in a single step. For that reason, it is considered as atom economicalreaction and "green chemistry". Asymmetric version of this reaction is alsobeing studies by organic groups for the synthesis of complex chiral compounds.In this respect, we have studied metal catalyzed cascade reaction of azomethineylides with electron defficient dipolarophiles by using chiral ligands with silvermetal. As the chiral ligands, amino alcohol based ferrocenyl aziridinyl methanol(FAM) and phosphorous based phosphino ferrocenyl aziridinyl methanol (PFAM)were used. These ligands have an advantage of being synthesized easily on agram scale starting from acryloyl ferrocene. Moreover, the yellow color offerrocene ease the purification by flash column chromatography. For the cascadereaction of azomethine ylides glycine methyl ester, aromatic aldehyde,dipolarophile, chiral ligand, and silversalt were mixed in the same reaction flask to form pyrrolidine derivatives. Although the optimization studies are stillgoing on and showed that, pyrrolidine derivatives can be obtained in goodyields and enantioselectivities. At this conference, synthesis of chiral ligandand pyrrolidine synthesis via azomethine ylide chemistry will be presented.

Keywords: *azomethine ylides; ligand effects; cascade;*

P-0810

ISOMERIZING OLEFINE METATHESIS

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Combining a metathesis catalyst with an isomerization catalyst can lead to a process in which unsaturated compounds are continuously converted into equilibrium mixtures of double bond isomers, which are concurrently undergoing olefin metathesis. Using highly active catalyst systems, the isomerizing olefin metathesis becomes an effective way to access defined distributions of unsaturated compounds from olefinic substrates. When ethylene is the cross metathesis partner, this isomerizing ethenolysis can be used for the shortening of olefin chains *via* stepwise cooperative isomerization and ethenolysis. Following this process, terminal olefins of higher value are obtained, with propylene being the only side-product. This new catalytic transformation is a potentially powerful tool for the transformation of easy available allylic compounds to the corresponding vinylic products. This concept is even viable for 4-phenyl-1-butene, which is converted to styrene *via* two subsequent isomerizing ethenolysis steps.

After systematic optimization of the reaction conditions using a Ru-catalyst, we explored the scope of this new transformation. Starting from low-price natural products, such as eugenol (16 € / 100 g), this method gives a direct access to valuable functionalized styrenes, such as 3-methoxyvinylphenol (500 € / 100 g), in very good yield and excellent selectivities. Under these reaction conditions, common functional groups, such as hydroxy groups, are tolerated. Phenolic substrates are challenging because of their tendency to polymerize.[1]

Compared to the traditional waste intensive methods like Wittig reactions, the transition metal catalyzed isomerizing ethenolysis is an atom-economical and environmentally friendly alternative for the synthesis of functionalized styrenes.[2]

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Keywords: *Metathesis; Isomerization; Fatty acids; Sustainable Chemistry;*

P-0811

COMPARING THE SPECTRAL PROPERTIES OF PYRENE PROBE, LABEL AND DERIVATIVE IN THE PRESENCE OF A NONIONIC SURFACTANT

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The behavior of pyrene as probe, label and derivative in octaethylene glycol mono n-dodecyl ether ($C_{12}E_8$), with or without polyacrylic acid (PAA), was mainly investigated by steady-state fluorescence spectroscopy. PAA was home labeled with pyrene (3% mol). As a probe, pyrene showed a typical behavior, irrespective of absence or presence of PAA; its emission spectrum presented five vibronic peaks for monomer and at higher wavelength and surfactant concentration, the peak corresponding to the sandwich excimer. As a label on PAA, the emission spectrum had higher intensity and the same shape, but 4 nm bathochromically shifted. The peak corresponding to the sandwich excimer appeared even in surfactant-free solution. The pyrene derivative was 4-(N',N'-diphenyl-hydrazine)-3,5-dinitrobenzoic acid 2-oxo-2-pyren-2-yl-ethyl ester. Its fluorescence emission spectrum had very low intensity, only two monomer peaks (I_1 and I_5), no sandwich excimer and a bathochromic shift of 9 nm. It was unexpected that, at the highest surfactant concentration used in this study, the derivative spectrum presented a 17 nm bathochromic shift. The data revealed that as a probe, pyrene is located in free or polymer-bound micelle, close to the core. As a label, it was first solubilized in the hydrophobic domains (it might force the polymer to shrink the coil) and, with surfactant addition, it was solubilized in micelles, closer to the ethylene oxide chains. The low intensity of the derivative fluorescence spectrum is due to the self-quenching favored by its structure. The derivative is probably located even closer to the palisade layer or actually hanged on it, which may explain the large bathochromic shift. As the nonionic micelle changes its shape and size, the derivative may be expelled somehow from the palisade layer. This approach may be useful in investigating such multi-assembled systems with the adequate fluorophore.

Keywords: *Fluorescent probes; Micelles; Polymers;*

P-0812

BIOPOLYMERIC MICROPARTICLES SYNTHESIZED BY INTERACTION OF CHITOSAN WITH ANIONIC SURFACTANTS

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Particles obtained by interaction of polymers with surfactants are important because they have multiple applications in environmental protection, pharmacy, medicine, etc. Among the candidates used to develop such particles a special attention was paid to chitosan (CS) biopolymer and sodium lauryl sulfate (SDS) surfactant. To extend the range of surfactants used to prepare polymer-surfactant (PS) particles we use in the present study the sodium laureth sulfate (SLES) and dioctylsodium sulfosuccinate (AOT) as anionic surfactants. Unlike SDS, SLES has ethylene oxide groups between the anionic group and the alkyl chain, which modify the hydrophobic character of the surfactant. Depending on the condition of synthesis two types of particles were obtained: **a**) microparticles – at atmospheric pressure, **b**) ultrafine particles – at high pressure. The microparticles are formed instantaneously at atmospheric pressure when drops of SLES come into contact with the CS solution. Depending on the weight ratio between chitosan and surfactant, the complex gel can take different forms: microcapsule that expels its content, stable microcapsule and deformed microcapsule.

To obtain ultrafine particles the SLES or AOT solution in contact with high pressure CO_2 were sprayed into chitosan solution bath, through a stainless steel capillary nozzle forming the chitosan-surfactant complex. It was found that increasing the spaying pressure the average diameter of ultrafine particles decreases.

The formation of CS-SLES and CS-AOT complexes was investigated by Fourier Transform Infrared (FTIR) Spectroscopy, whereas scanning electron microscopy was used to characterize the morphology, size and shape of particles. FTIR spectrum proves the interaction between the sulfate group of SLES or AOT and the ammonium group of CS. The microparticles are quasi-spherical but some of them can take the form of pellets. The study allowed us to understand the interaction between CS and SLES, and to suggest a scheme of molecular complex formation by cross linking.

Keywords: *Surfactants; Polymers;*

P-0813

ENVIRONMENTALLY BENIGN METAL-FREE DECARBOXYLATIVE ALDOL AND MANNICH REACTIONS

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Organocatalysis stands as an eco-friendly and cost-effective methodology for the creation of carbon-carbon, carbon-heteroatom and carbon-hydrogen bonds.

β-hydroxyester is a structural moiety frequently encountered in many bioactive compounds and natural products[1]. Most of the methods to synthesize *β*-hydroxyesters rely on organometallic chemistry and the use of metal complexes (Reformatsky [2], aldol-type reactions[3]) in particular when the control of the stereochemistry is needed. Therefore, in those conditions, anhydrous solvents, low temperature, and the presence of a strong base are often required.

The aim of this work is to develop an efficient methodology affording *β*-hydroxyesters and *β*-aminoxyesters under metal-free conditions. We describe herein a detailed study of the decarboxylative aldol and mannich reactions between a non-substituted ester hemimalonic acid and aldehydes and imines, in the presence of an achiral amine. The methodology was extended to *α*-substituted hemimalonic acids giving access to *α*-substituted-*β*-hydroxy/aminoesters.

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Keywords: *Organocatalysis; Decarboxylation; Mannich; aminoacids; aldol reaction;*

P-0814

WATER SOLUBLE N-HETEROCYCLIC CARBENE GOLD COMPLEXES

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In 1991 Arduengo[1] isolated the first “free” N-heterocyclic carbene. Since then the interest in NHC transition metal complexes increased rapidly due to their σ-donating properties and their broad variation range in steric features which allow an excellent stabilization of the metal center and an enhancement of their catalytic activity.[2, 3]

In our investigations, water soluble NHC gold catalysts will be synthesized. During the last two decades, water has gained great interest as a solvent. Low costs as well as environmental and safety aspects are the main advantages of water. Therefore, water-based catalysts are required.[4] The introduction of a water soluble residue at the NHC ligand like an ammonium salt or a sulfonate group is a potential approach. These residues are already known from phosphine ligands.[5] However, there are just a few water soluble NHC complexes so far.[6-9]

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Keywords: *Carbene ligands; Gold; Nitrogen heterocycles; Ligand design; Water chemistry;*

P-0815

PROTON TRANSFER IN CALCIUM-REGULATED BIOLUMINESCENT REACTIONS: PECULIARITIES OF FLUORESCENCE SPECTRA

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Calcium-regulated bioluminescent reactions catalyzed by photoproteins are responsible for bioluminescence of marine coelenterates. Photoprotein is a stable enzyme-substrate complex consisting of a single polypeptide chain and an oxygen “pre-activated” substrate, 2-hydroperoxycoelenterazine which is tightly but noncovalently bound within a hydrophobic cavity inside the protein. Addition of calcium ions to photoprotein triggers a bioluminescent reaction resulting in light emission with λ_{max}=485 nm. The product of the bioluminescent reaction (enzyme-bound chromophore, coelenteramide) is a fluorescent protein; It is called ‘discharged’ photoprotein. Obelin isolated from hydroid *Obelia longissima* is one of the most studied among photoproteins. Obelin is stable and nontoxic natural complex; its spectra, and hence, color of luminescence, are variable. This is why it is considered as perspective bioluminescent and fluorescent marker for biological and medical investigations *in vitro and in vivo*. Therefore the fluorescent peculiarities of obelin are of high interest.

Spectra of obelin bioluminescence and discharged obelin photoluminescence are wide and complex. Photoluminescence spectra depend on external physico-chemical conditions of obelin solution (pH, calcium concentration, and temperature), but bioluminescence spectra do not.

The spectra were deconvolved into spectral components using Gauss distribution and method of second derivative. Spectral components were attributed to protonated and several deprotonated forms of coelenteramide with different acidity in its fluorescent states. Effectiveness of proton-transfer process depends on conformation of obelin active center - distance between coelenteramide and proton-accepting group of amino acid environment. We suggest that discharged obelin might form several conformations depending on physico-chemical conditions. For example, analysis of photoluminescent spectra of discharged obelin under different calcium concentration revealed considerable spectral changes at $[Ca^{2+}] \approx 0.5$ µM, this pointing to enzymatic conformational transition in discharged obelin. Meanwhile only one conformation of obelin is responsible for bioluminescence under different conditions.

Keywords: *Fluorescence spectroscopy; Proton transport; Photoprotein;*

P-0816

NEW SAMARIUM DIIODIDE MEDIATED CASCADE REACTIONS – APPROACHES TOWARDS STRYCHNOS ALKALOIDS

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The indole ring system is probably the most ubiquitous heterocycle in nature and has become an important structural component in many pharmaceutical agents.[1] In our group indole derivatives are used in SmI_2- mediated reductive 6- to 8-*exo-trig* cyclizations in order to build up highly functionalized polyheterocycles.[2] Recently, various substitution patterns of the indole moiety and different electrophiles as trapping reagents for the *in situ* generated samarium enolate have been investigated and the desired tricyclic compounds were obtained in high yields as single diastereomers. Now, we report a novel cascade reaction mediated by SmI_2 which leads to synthetically interesting tetracyclic indole derivatives and features the generation of two new rings and three stereogenic centers, including a new quarternary center.

The tetracycle was an ideal candidate for a formal total synthesis of Strychnine. A total synthesis with the pentacyclic key building block was already described by Rawal in 1994.[3] Herein, we will describe our approach towards the key building block, finalizing a very short formal synthesis of Strychnine.[2f]

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Keywords: *Samarium; Radicals; Cyclization; Natural products;*

P-0817

SYNTHESIS OF NITROGEN-CONTAINING GRAPHENE NANORIBBONS

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The replacement of one or multiple carbon atoms in a polyaromatic hydrocarbon (PAH) clearly changes its optoelectronic properties. This is not only a very interesting topic of heteroaromatic chemistry but also a challenging task in the field of materials science, regarding nitrogen-containing graphitic materials. For example such metal-free materials have proven to be promising candidates for oxygen reduction catalysts at cathodes of fuel cells.

As a synthetic group the tools of organic chemistry allow us to create nanographenes, as well as longitudinally extended graphene nanoribbons (GNRs) in a variety of topologies. For the fabrication of GNRs we applied techniques of solution or surface-assisted polymerization of dihalogenated tetraphenyltriphenylene derivatives, followed by cyclodehydrogenation to give the planarized graphitic material. In this study, we utilized this method and introduced nitrogen atoms to GNRs at designed positions by designing appropriate precursors. All the nitrogen atoms were located at the periphery, which could be controlled to be uniform pyrimidine or pyridine type structure. This is in sharp contrast to other protocols such as pyrolysis of nitrogen enriched precursors and treatment of graphene with nitrogen sources like ammonia, which give structurally undefined nitrogen-containing graphenes. Furthermore, it is possible by this method to compare the nitrogen doped GNRs with their parent GNRs and to evaluate the effect of the nitrogen atoms on their properties. By statistical copolymerisation of doped and undoped monomers it is also possible to adjust the nitrogen content without changing the structure of the carbon framework.

In summary we could extend our established method of bottom-up synthesis to a new class of nitrogen containing GNRs.

Keywords: *Graphene; Nitrogen;*

P-0818

REDOX MODULATION OF THE SHUTTLING MOTION IN A TRISTABLE [2]ROTAXANE

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The investigation on mechanically interlocked architectures has produced a number of programmed systems for performing induced movements at will.[1] In this context, two-station [2]rotaxanes involve a privileged place due to their potential use as molecular devices.[2] In a previous work we proved that azodicarboxamide groups can act as efficient templates for the assembly of hydrogen-bonded rotaxanes and can be employed for the building of chemically-driven molecular shuttles.[3] Herein we describe the submolecular translational movement in novel hydrogen-bonded [2]rotaxanes containing benzylic amide macrocycles and two azo/hydrazodicarboxamide binding sites.[4] We disclosed that the modulation of the oxidation level of these systems give rise to interlocked molecular architectures featuring novel dynamics of significance for the tuning of distance and/or time dependent properties.

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Keywords: *Rotaxanes; Noncovalent interactions; Azo compounds; Molecular dynamics; Redox chemistry;*

P-0819

NON-COVALENT INTERFERENCE ON THE MACROCYCLE ROTATION OF HYDROGEN BONDED [2]ROTAXANES

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Controlling motion in interlocked molecular architectures has been a trending subject during the last years[1] for the scientific community and, mainly, for researchers interested on the modelling of the biological machinery and the development of stimuli-responsive molecular devices.[1c]

In this communication we disclose that the incorporation of cyclohexylmethyl stoppers on the succinamide-based binding site of a [2]rotaxane has a clear effect over the macrocycle rotation[2] through the establishment of non-covalent interactions This study was supported by a dynamic ^{1}H NMR study performed with a set of five hydrogen bonded [2]rotaxanes and the molecular structure in the solid state of one of these interlocked molecules.[3]

Acknowledgement: *This work was supported by the MICINN (Projects CTQ2008-05827/BQU and CTQ2009-12216/BQU), the MINECO (Project CTQ2012-36158/BQU) and the Fundación Séneca-CARM (Project 08661/PI/08). J.B. thanks to the MICINN for a Ramón y Cajal contract (RYC-2008-02647), co-financed by the European Social Fund.*

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Keywords: *Rotaxanes; Self-assembly; Noncovalent interactions; Molecular dynamics; X-ray diffraction;*

P-0820

CHIRAL IMIDATE-PHOSPHANES: PROGRESS IN THEIR SYNTHESIS AND APPLICATION AS N,P-LIGANDS

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Chiral imidate-phosphanes were recently developed in our lab as a new type of P,N-ligands, easily accessible via a one-step procedure starting from an imidate precursor and a commercially available chiral aminophosphane.[1]

We wish to report here on the performance of these ligands in the Pd(0)-catalyzed allylic alkylation and amination and the Ir(I)-catalyzed asymmetric hydrogenation of unfunctionalized olefins.[2]

The observed performance of our imidate-phosphane ligands with various carbon and amine nucleophiles in the Pd(0)-catalyzed allylic alkylation and amination appeared to be good to excellent (yields up to 99% and ee's up to 99%). Moderate to very good results (yields up to 99.9% and ee's up to >99%) were obtained with our imidate-phosphane ligands in the Ir(I)-catalyzed asymmetric hydrogenation of unfunctionalized olefins.

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Keywords: *Asymmetric catalysis; Asymmetric synthesis; Hydrogenation; Palladium;*

P-0821

AROMATIC CARBOXYLIC ACIDS IN DECARBOXYLATIVE ETHERIFICATION

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Transition metal-catalyzed decarboxylative coupling reactions have emerged as a powerful strategy to form carbon–carbon or carbon–heteroatom bonds starting from carboxylic acids. In these reactions, C–C bonds to carboxylate groups are cleaved, and in their place, new carbon–carbon bonds are formed. Decarboxylative cross-couplings constitute advantageous alternatives to traditional cross-coupling or addition reactions involving preformed organometallic reagents. While the overwhelming majority of decarboxylative couplings of aromatic carboxylates proceed with formation of C–C bonds, the only example of C–heteroatom bond forming reactions are restricted to C–S and C–Se bond formation.

Here we present the decarboxylative C–O coupling as a practical access to alkyl-aryl and diaryl ethers avoiding the use of the often expensive organic halide and boronic acid precursors. Alkyl aryl- or diaryl ethers are synthesized starting from easily available aromatic carboxylic acids and alkoxysilanes or aryl boranes respectively. The reaction occurs under aerobic conditions in the presence of silver carbonate as the decarboxylation catalyst and copper acetate as the cross-coupling catalyst. Thus, aromatic carboxylates with various electron-withdrawing and –donating groups in the *ortho* position e.g. nitro, methoxy, dimethylamino, sulfonyl, chloro, fluoro, trifluoromethyl or phenyl groups, were successfully converted to the corresponding aryl ether. On the other hand, for carboxylates with a low tendency to extrude carbon dioxide, an alternative pathway consisting of *ortho* functionalization followed by protodecarboxylation has been shown to be functional, so that the ether group is installed in the *ortho* rather than the*ipso* position of the former carboxylate group.

This approach combines the key benefit of regiospecificity with the broad availability, low cost, and easy handling of carboxylate substrates and therefore serves as an attractive alternative to the traditional Buchwald-Hartwig and Chan-Evans-Lam reactions.

Keywords: *C-C activation; cross-coupling; regioselectivity; copper; silver;*

P-0822

DYNAMIC KINETIC RESOLUTION OF METHYL 2,3-DIHYDROBENZO[B]FURAN-3-CARBOXYLATE AND ETHYL 5-CHLORO-2,3-DIHYDROBENZO[B]FURAN-3-CARBOXYLATE

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Enzymatic kinetic resolution is a powerful tool for separating enantiomers of a racemic mixture. A severe limitation is the maximum theoretical yield of 50% in all cases, unless racemisation of the substrate is possible. The dynamic enzymatic kinetic resolution could in these cases overcome the disadvantage and would thus furnish products with a very high enantiomeric excess and in high yield. Hydrolases such as lipases are still the preferred biocatalysts to establish dynamic enzymatic kinetic resolution since they are readily available and – concerning the reaction conditions – show considerable flexibility.[1]

Herein we report a method for the kinetic resolution of racemic methyl 2,3-dihydrobenzo[*b*]furan-3-carboxylate and its chlorine derivative methyl 5-chloro-2,3-dihydrobenzo[*b*]furan-3-carboxylate. After establishing a successful biocatalytic system with outstanding results concerning *ee* and yield, dynamic, enzymatic, kinetic resolutions were investigated to increase yields up to more than 50 %. The compounds of interest were known precursors for analgesic agent 7-benzoyl-5-chloro-2,3-dihydrobenzo[*b*]furan-3-carboxylic acid (BRL 37959).[2]

For improving enzyme screening, reversed phase HPLC with CD detector was used to determine *ee* during screening. This method allows high throughput screening because of its time advantage compared to normal phase chiral HPLC. Especially to find an enzyme that hydrolyses selectively ethyl 5-chloro-2,3-dihydrobenzofuran-3-carboxylate which affords better yields than the corresponding methyl ester when carrying out *Friedel-Crafts* acylation to come to ethyl 7-benzoyl-5-chloro-2,3-dihydrobenzo[*b*]furan-3-carboxylate, which can easily be hydrolysed under acidic conditions to afford analgesic agent BRL 37959.

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Keywords: *dynamic kinetic resolution; chemoenzymatic; analgesic agent;*

P-0823

DIASTEREOSELECTIVE SYNTHESIS OF NEW OPTICALLY ACTIVE 1-(SUBSTITUTED ARYL)PYRROLE DERIVATIVES

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Multisubstituted 1-arylpyrroles are known intermediates of biologically active compounds (mytomycine analogs, pyrrolobenzoxazepines, neopyrolomycine). Synthesis of these compounds via classical methods usually results in low yields because of the acid sensitivity of the pyrrole ring. Application of organometallic reagents can help one to get rid of that problem if highly selective mono- and dimetallation methods were available for these types of compounds.

First members of C_1 symmetric atropisomeric 1-arylpyrrole derivatives were prepared by our research group about 10 years ago[1]. Some of these derivatives can be applied as chiral ligands too. Later we prepared the optically pure atropisomeric 1-(2-carboxymethyl-6-ethylphenyl)-1H-pyrrole-2-carboxylic acid by consecutive dimetalation of 1-(2-ethylphenyl)-1*H*-pyrrole with activated organometallic type base and solid carbondioxide to provide racemic derivative followed by the resolution of dicarboxylic acid with *(S)*-1-phenylethylamine[2]. Herein we report on the examination of the regioselective metalation and stereoselective derivative formation of the atropisomeric dicarboxylic acid. The new derivatives were obtained in a diastereoselective way and in good yields by consecutive monometalation of the acid with LiDA-KOR followed by the reactions with different reagents (for example iodomethane, benzaldehyde, dimethylformamide, isobutyl bromide, benzyl bromide, etc.).

Absolute configurations of successfully prepared (+)-1-(2-(1-carboxyethyl)-6-ethylphenyl)-1H-pyrrole-2-carboxylic acid was determined using single crystal X-ray diffraction measurements.

The substituted dicarboxylic acids were converted into monoesters in two different ways: selective hydrolysis of the diester, which was formed with an excess of thionyl chloride in ethanol or selective monoesterification.

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Keywords: *Regioselectivity; Diastereoselectivity; Metalation;*

P-0824

BINDING MODE INFLUENCE ON GAS-PHASE FRAGMENTATION OF ADAMANTYLATED BISIMIDAZOLIUM@CUCURBIT[7]URIL COMPLEXES

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Within two past decades, the host-guest chemistry of cucurbit[n]urils (CBs) and various guests has been extensively studied in solution as well as in the gas phase. We prepared new adamantylated bisimidazolium (BIM) salts and examined their binding behavior towards CB7 in the gas phase using an ion trap instrument equipped with electrospray ion source. Two distinct binding modes may be supposed for our systems. In the first class of complexes, the adamantane moiety is arranged inside the interior cavity of CB7 and only one CB7 carbonyl portal is occupied by positively charged imidazolium ring. If it is sterically allowed, the CB7 unit may slip over the BIM scaffold to form the complex of the second class with both CB7 carbonyl portals occupied by imidazolium rings. Sole BIM dications decomposed in concert with electrostatic repulsion to produce two singly charged fragments upon collision induced dissociation (CID) conditions. Similarly, the complexes of BIM bearing bulky substituents dissociated to singly charged axel residue and aggregate of 1-adamantylmethyl cation with CB7. In contrast, some BIMs complexed to CB7 released neutral fragment (1-adamantylcarbene) to form doubly charged aggregate of CB7 and axel residue. Furthermore, the subsequent releasing of the second 1-adamantylcarbene was observed. This unexpected fragmentation occurred only when the slippage of CB7 unit over the BIM axel is sterically allowed. This phenomenon may be employed as an efficient tool for binding mode clarification using mass spectrometry.

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Keywords: *gas-phase reactions; host-guest system;*

P-0825

TRACELESS TOSYLHYDRAZONE-BASED TRIAZOLE FORMATION: TOWARDS A VIABLE AND ROBUST ALTERNATIVE FOR THE COVALENT LABELING OF VARIOUS BIOMOLECULES

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Traceless Tosylhydrazone-based Triazole formation (Sakai reaction) can be readily achieved by reacting primary amines with functional α,α-dichlorotosylhydrazones under ambient conditions. This fast and efficient alternative to the copper-assisted azide-alkyne cycloaddition (CUAAC) and strain-promoted azide-alkyne cycloaddition (SPAAC) affords, exclusively, 1,4-substituted triazole "click-products" with high stereoretention. Moreover the observed versatility and chemoselectivity of the here presented metal-free triazole formation methodology led us to the conclusion that primary amines, inherent to many natural products and biomolecules, should be applicable as functional handles for further modifications (e.g. fluorescent labeling, biotinylation). Besides the synthesis of various functional α,α-dichlorotosylhydrazones, first attempts regarding the bioapplicability of the Sakai reaction will be discussed.

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Keywords: *Click Chemistry; Heterocycles; Hydrazones;*

P-0826

A SELECTIVE CONVERSION OF BENZYLIC ALCOHOLS TO THE CORRESPONDING CARBONYL COMPOUNDS BY MEANS OF AN AG(III) AND CU(III) COMPLEXES

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The oxidation of alcohols into aldehydes and ketones is a ubiquitous transformation in organic chemistry and numerous oxidizing agents are available to effect this key reaction. This reaction raises continuous interest, but most of these reactions have not been applied to sensitive natural polyfunctional products. In recent years investigators have been increasingly interested in studies of unusual oxidation states of transition metals such as Cu(III), Ni(III), Ni(IV), Ag(III). We now have looked more closely at the possibility of preparing carbonyl compounds with the aid of Ag(III) and Cu(III) complexes, partly because it is unusual for Ag and Cu species to have charge +3, which means it can easily change charge; partly because complex being easily made of inexpensive chemicals.[1, 2]

Investigations have been carried out with some potentially oxidable substrates which contains different type of hydroxyl group in the molecule like D-(-)-*threo*-2-dichloroacetamido-1-(4--nitrophenyl)-1,3-propanediol(chloramphenicol), (1R,2R)-(-)-2--amino-1-(4-nitrophenyl)-1, 3 -propanediol, (S)-1-phenyl- 1, 3 --propanediol and Ag(III) and Cu(III) complexes. The method gives the possibility of selective oxidation of benzylic hydroxyl groups in polyhydroxyl compounds in good yields. Such systems occur in nature and medicine and thus there is considerable interest in devising synthetic methods for their regioselective oxidation.

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Keywords: *Alcohols; Aldehydes; Ketones; Oxidation;*

P-0827

KILOGRAM PRODUCTION OF CORANNULENE: OPTIMIZATION AND POTENTIAL APPLICATIONS

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Corannulene was first synthesized in 1966 in 16 steps with less than a 1% yield.[1] This synthesis on milligram-scale, albeit pioneering, was not suitable for preparing enough material for further application. Improvements in the synthesis of corannulene have opened the door for a series of mono-, di-, tetra-, penta-, hexa- and deca- substituted derivatives on gram scale.[2] These derivatives can be used as a template for a variety of higher order structures, such as graphite tubes/caps, liquid crystals, dendrimers, polymers, cruciforms, cyclophanes and molecular clefts. To exploit the materials chemistry of such derivatives, a chemical process for production of corannulene on kilo scale would be advantageous.

An efficient entry process for the synthesis of corannulene has been demonstrated on kilogram scale.[3] Compared to the discovery and gram-scale syntheses, the amounts of solvents and reagents per gram of product were greatly reduced. Priority was given to implement the least toxic agents possible. Improvements in the purification of products obviated the need for column chromatography, alleviating four chromatographic operations. A new reduction method for the final step of the synthesis decreased reaction time from 6 to 0.5 days, and avoided the use of 100 equiv of zinc metal. The process now comprises nine steps, each of which runs smoothly at 100-L scale with a charging of 3–12 kg of educt. A total of 1.3 kg corannulene was isolated. This kilogram-scale process reduces material costs by over 2 orders of magnitude compared to that for the published gram-scale syntheses.

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Keywords: *hydrocarbon; polycycles;*

P-0828

ASYMMETRIC DIETHYLZINC ADDITION TO N-SULPHONYLIMINE

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Design of new chiral ligands for asymmetric synthesis is important. The ligand should be economical and efficient in enantioselective transformations. For the synthesis of some natural products and biologically active compounds optically active amines are used as important intermediates. For this reason, it is important to develop new catalyst system which can produce optically active amines in an economical and efficient way. Our group developed ferrocenyl aziridinyl methanol (FAM), phosphino ferrocenyl methanol (PFAM), and phosphineoxy aziridinyl phosphonate (POAP) ligands and used successfully for the enantioselective synthesis of organic compounds. These chiral ligands can also serve as organocatalysts for the synthesis of organic compounds. In this study, these ligands were tested as chiral catalysts for enantioselective synthesis of amines. For this purpose, diethylzinc was added to N-sulphonylimine synthesized from aromatic and aliphatic aldehydes in the presence of FAM and PFAM ligands. Although ligand screening and optimization studies are continuing, the results obtained so far showed that chiral amines can be obtained in good yields and acceptable enantioselectivities. During these studies, we have developed an excellent method for the synthesis of starting N-sulphonylimine. At this conference synthesis of N-sulphonylimine, chiral ligands and details of asymmetric diethylzinc addition to imines to form chiral amines will be presented.

Keywords: *Imines; Organometallic; Asymmetric synthesis;*

P-0829

SYNTHESIS AND USE OF NEW PHOSPHINEOXY AZIRIDINYL PHOSPHONATES (POAP) AS ORGANOCATALYSTS IN ASYMMETRIC PHOSPHONYLATION OF ALDEHYDES

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α-Hydroxy phosphonates are biologically active compounds.[1] Enantioselective synthesis of these compounds is studied by a significant number of scientists by employing dialkyl phosphites known as Pudovik-type reaction. On the other hand, only one group studied the enantioselective synthesis of α-hydroxy phosphonates by employing trialkyl phosphites known as Abramov-type reaction in the presence of diphosphine oxy chiral Lewis bases.[2] In this respect, we tried newly synthesized phosphine oxy aziridinyl phosphonates (**POAP**) as Lewis bases for the Arbuzov-type reaction. Reaction of trialkyl phosphite with aldehydes in the presence of $SiCl_4$ and chiral Lewis base produced desired α-hydroxy phosphonates in very good yields (up to 99%) but moderate enantioselectivities (highest 43%). Although the enantioselectivity is low, initial results are encouraging. Because, literature also reports similar enantioselectivities for the same reaction. We haven't finished the optimization studies therefore more experiments are on the way for improving the enantioselectivy. The details of this study will be presented at this conference.

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Keywords: *Silicon based; Abramov-type phosphonylation; Organocatalyst; Hydroxy phosphonate; Asymmetric reaction;*

P-0830

TOTAL SYNTHESIS OF DIPHOSPHOINOSITOL POLYPHOSPHATES (PP-INSP$_5$)

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Secondary messengers permit the communication within and between cells and are crucial for the maintenance of life. Diphosphoinositol polyphosphates (PP-InsP$_5$) belong to these signaling molecules and are important in different cellular processes including signal transduction, vesicle trafficking, cell division and apoptosis.[1] Recently, pyrophosphorylation of proteins has been described, but the function of this post-translational modification is still unknown.[2] Therefore, an efficient synthesis of PP-InsP$_5$ is necessary to study their unique mode of action. Due to the structure of *myo*-inositol, many different phosphorylated derivatives are possible and those found in nature have distinct functions in cellular systems. Different syntheses of enantiomerically pure inositol polyphosphates have been reported[3] and among these asymmetric phosphorylation is an outstanding way to introduce a phosphate group in a specific position in the structure of *myo*-inositol. We will report the synthesis and application of C_2 symmetric phosphoramidites to desymmetrize different inositol derivatives leading to diastereoisomeric mixtures. In some cases it was possible to separate the mixtures by simple column chromatography obtaining diastereomerically pure compounds. Also different phosphoramidite activators and solvents have been evaluated, demonstrating their importance in the selectivity of the phosphorylation. These results represent a new approach in the envisaged total syntheses of PP-InsP$_5$ as well as the starting point for the development of efficient reagents for asymmetric phosphorylation and pyrophosphorylation.

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Keywords: *phosphorylation; synthetic methods; total synthesis; asymmetric synthesis; medicinal chemistry;*

P-0831

SYNTHESIS OF PORPHYRIN-STEROID CONJUGATES

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The aim of this work was to synthesize and subsequently try on self-assembly properties of several porphyrin-steroid conjugates. Bile acids are a group of steroids with amphiphilic and detergent properties that are caused by a convex hydrophobic upper side, a concave hydrophilic α-side and a negatively charged side-chain[1]. Due to their large, rigid, curved steroidal skeletons and amphiphilicity, together with their availability and low cost are bile acids ideal building blocks for the design of novel molecular and supramolecular assemblies for molecular recognition[2]. Not only fluorescent activity is provided by porphyrin, these pyrrole macrocycles are recently studied for their use in photodynamic therapy[3] as well.

Several porphyrin-steroid conjugates with ester, amide and ether bound were prepared and their properties are studied now. Resulting compounds show aggregation properties – extensively investigated nowadays because of their possible technological applications. Aggregation experiments were carried out according to known procedure[4]. Hence, using of DMSO/water solution solvent-promoted aggregation of amphiphilic porphyrin derivative was achieved. This composition induces efficient porphyrin self-aggregation process to form J-type aggregates, observed by the broadening and bathochromic shift of the Soret band.

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Keywords: *Aggregation; Steroids; Porphyrinoids;*

P-0832

WATER-SOLUBLE PHTHALOCYANINES FOR PHOTODYNAMIC THERAPY

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Photodynamic therapy (PDT) is one of the alternative approaches for cancer treatment. PDT uses a combination of three essential components: photosensitizer, oxygen and light. Unsubstituted phthalocyanines (Pc) are completely water-insoluble and they tend to aggregate in solution. These properties are limiting factors for use in PDT. Presence of cationic substituents on periphery of Pc macrocycle generally increases water solubility and limits the aggregation. In this study, cationic magnesium, zinc and metal free Pcs substituted in peripheral (β) or non-peripheral (α) positions on macrocycle were prepared.

Pcs are usually synthesized by cyclotetramerization reaction from corresponding precursors, substituted phthalonitriles. Thus, 4,5-bis[2-(diethylamino)ethylsulfanyl]phthalonitrile was prepared by nucleophilic substitution from 4,5-dichlorophthalonitrile. Similarly, 3,6- disubstituted phthalonitrile arose from 3,6-dihydroxy phthalonitrile after conversion of hydroxyl groups to tosyl groups. Cyclotetramerization of these precursors was accomplished with magnesium butoxide as an initiator of the reaction. Magnesium Pcs prepared in this way were were converted to metal-free Pcs using 1% hydrochloric acid. Metal-free Pcs reacted with anhydrous zinc acetate in pyridine to form corresponding zinc complexes. Finally, peripheral tertiary amino groups of these complexes of Pcs containing were quarternized with ethyliodide.

The Pcs substituted in α positions did not aggregate in water in wide range of concentrations. Moreover, cationic zinc Pc with substitution in α positions showed excellent absorption and photochemical properties (λ_{max} 756 nm and quantum yield of singlet oxygen 0.91). Therefore this Pc could become a new potential photosensitizer for PDT.

Keywords: *Phthalocyanines; Singlet oxygen; Fluorescence; Cancer;*

P-0833

INSIGHTS ABOUT THE STRUCTURE OF A POSSIBLE HIGH-ENERGY INTERMEDIATE OF THE CHEMILUMINESCENT PEROXYOXALATE REACTION

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The peroxyoxalate system is one of the most efficient nonenzymatic chemiluminescent reactions known, showing quantum efficiency of up to 50%. The bluish light, first observed by Chandross from the reaction between oxalyl chloride and hydrogen peroxide in the presence of 9,10-diphenylanthracene (DPA), has inspired generations of scientists to investigate the reaction mechanism and to search for new experimental conditions to improve emission efficiency. The exact mechanism of the chemiexcitation process has been determined, but the structure of the high-energy intermediate responsible for this chemiexcitation remains not fully determined.

Bimolecular interaction of this HEI, accumulated in the reaction of oxalyl chloride with hydrogen peroxide, with an activator (highly fluorescent aromatic hydrocarbons with low oxidation potential) added in delay shows unequivocally that this intermediate is responsible for chemiexcitation of the activator. Activation parameters for the unimolecular decomposition of this intermediate ($\Delta H^{\neq} = 11.2$ kcal mol^{-1}; $\Delta S^{\neq} = -23.2$ cal mol^{-1} K^{-1}) and for its bimolecular reaction with 9,10-diphenylanthracene ($\Delta H^{\neq} = 4.2$ kcal mol^{-1}; $\Delta S^{\neq} = -26.9$ cal mol^{-1} K^{-1}) show that this intermediate is much less stable than typical 1,2-dioxetanones and demonstrate its highly favored interaction with the activator. Therefore, it can be inferred that structural characterization of the high-energy intermediate in the presence of an activator must be highly improbable.

Kinetic studies of the imidazole catalyzed chemiluminescent reaction of a series of substituted peroxalic acids, postulated intermediates of the PO system, yielded a linear free-energy correlation of the catalytic rate constants with Hammett parameters ($\rho = +2.0 \pm 0.2$ and $\beta_{LG} = -1.1 \pm 0.1$) which are compatible with a base-catalyzed concerted intramolecular substitution reaction in the chemiluminescent pathway of this transformation. Therefore, these data indicate the cyclic peroxydic carbon dioxide dimer 1,2-dioxetanedione as the most probable high-energy intermediate in the peroxyoxalate reaction.

Keywords: *organic peroxides; chemiluminescence; peroxyoxalate;*

P-0834

SOME AQUEOUS CHEMISTRY OF THE THIOPHOSPHORYL GROUP

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The Aqueous Reduction of Azides Using Sodium Thiophosphate: We present a clean, aqueous method for the conversion of azides to amines with trisodium thiophosphate as the reducing agent.[1] The transformation is shown to be effective on a range of alkyl and aryl substrates.

Thiophosphoryl 'Click' Chemistry: Our group has developed a one-pot synthesis allowing two organic groups to be conjugated by a thiophosphoramidate linker.[2] The reaction has been tested on a range of substrates and has been found to be widely applicable. The method shows high levels of conversion and generates innocuous by-products. This chemistry has potential as a mimic of phosphate-containing biological systems, and as an example of this, we have applied the methodology to the synthesis of a thymidyl-(3'-5')-thymidine thiophosphoramidate analogue with a view to studying the hydrolytic properties of this system.

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Keywords: *Aqueous; Azide; Phosphate; Thiophosphate;*

P-0835

REACTIVITIES OF ETHYL ARYLACETATE ANIONS

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The anions of ethyl arylacetates are frequently used as nucleophiles in Michael additions and Claisen condensations. Furthermore, they can easily be alkylated or added to carbonyl groups, imines, or acetylenes leading to a wide variety of products of biological and medicinal interest.

Kinetic investigations of the reactions of the anions of ethyl arylacetates with quinone methides and diethyl benzylidenemalonates in DMSO allowed us to quantify their nucleophilic reactivities according to the linear free energy relationship eq [1], in which electrophiles are characterized by one parameter E and nucleophiles are characterized by the solvent-dependent parameters s_N (sensitivity) and N (nucleophilicity).[1]

$$\lg k_2(20\ °C) = s_N(N + E)\ (1)$$

Our investigations show that the nucleophilic reactivities of these compounds are highly affected by the substitution pattern of the aromatic ring. Their nucleophilicities are comparable to those of the anions of phenyl acetonitriles.[2] The title compounds thus belong to the most reactive nucleophiles so far studied by our group and can be used to characterize very weak electrophiles.

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Keywords: *Kinetics; Carbanions; Linear free energy relationship;*

P-0836

SYNTHESIS AND EVALUATION OF TRIAZOLE-LINKED CALIX[4]ARENE IONOPHORES

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Over the past decade the Cu(I)-catalyzed dipolar azide-alkyne cycloaddition (CuAAC) leading to 1,2,3-triazoles has attracted an enormous interest as one of the most useful and valuable example of click chemistry. In calixarene chemistry CuAAC has also been applied for the easy access to sophisticated large molecules such as triazole-linked calix[4]arene ionophores often supplied with chromo/fluorogenic moieties. Interstingly, the majority of these ligands has a common binding site comprised of two distal triazole- and two OH groups on the lower rim of the calixarene framework.

So far only one type of the tetrasubstituted derivatives has been reported, therefore we aimed at increasing the choice of ionophores in this field by synthesizing a series of ligands either with the combination of triazole- and (thia)carboxamide/ester groups or with introducing four triazole ligating groups at the lower rim in order to find metal ion-selective molecules suitable for developing new potentiometric sensors.

The majority of the new molecules were tested by competitive MS measurements in the presence of a series of mono- and divalent metal ions to estimate the relative complexation abilities. Subsequently, PVC membrane electrodes (ISE) were fabricated to determine the potentiometric ion-selectivity coefficients.

Keywords: *Click chemistry; Calixarenes; Ionophores; Mass spectroscopy; Molecular recognition;*

P-0837

FUNCTIONALIZATION OF CORANNULENE VIA DIRECT IRIDIUM-CATALYZED BORYLATION

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Over the past decade, significant effort has been invested in the derivatization of polyaromatic hydrocarbons, such as corannulene, in order to introduce functionality and thus provide building blocks for more complex architectures.[1] Due to its five-fold symmetry, corannulene is a suitable core element of higher-order supramolecular structures such as host-guest complexes[2], dendrimers[3], and liquid crystals[4]. The conventional method for functionalizing corannulene, while keeping the five-fold symmetry, has been to convert it to 1,3,5,7,9-pentachlorocorannulene, which may then undergo further alkylation or arylation reactions.[5, 6] However, this approach suffers from several challenges including poor solubility, difficult purification, and low reactivity of aryl chlorides toward substitution. To overcome these problems, a new synthetic strategy has been established for the functionalization of corannulene using iridium-catalyzed borylation under basic conditions.[7, 8] The reaction proceeds via direct C-H activation, affording highly soluble 1,3,5,7,9-pentakis(Bpin)corannulene in 65–70% yield. Optimization studies as well as the properties of the newly synthesized compound and its reactivity toward Suzuki cross-coupling reactions will be presented.

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Keywords: *corannulene; functionalization; borylation; C-H activation; polyaromatic hydrocarbon;*

P-0838

FUNCTIONAL LC ELASTOMERS: TOWARDS ARTIFICIAL ACTUATORS

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Liquid crystal elastomers (LCEs) are materials with uncommon elastic properties that combine the orientational ordering properties of liquid crystalline systems with the rubbery elasticity of polymer networks.[1] The ability of these materials to change their shape and size reversibly by inducing disorder in the liquid crystalline structure at the nematic – isotropic phase transformation (triggered by temperature) makes them attractive for use as actuating materials like sensors, valves and electronics. However, the study of such reversible systems is limited by their difficult syntheses and new methodologies are required. In this work we have developed a new strategy based on the Cu catalyzed 1,3 dipolar cycloaddition between azides and alkynes[2] in a one pot process for the preparation of a variety of liquid crystal polymers (LCPs) and LCEs. In the context of this approach, a collection of calamitic and bent core monomers bearing alkyne groups have been synthesised and reacted with diazide spacers and multivalent alkyne substituted cross linkers to form LCPs and LCEs. A series of copolymers has also been prepared by using monomeric blends composed of mesogens of different shapes in order to prepare systems exhibiting nematic phases over wide but accessible temperature ranges.[3] The results indicate that our strategy can be generally applied to the preparation of polymeric and elastomeric materials since it leads to high polymer conversions, short reaction times, and simple purification techniques.

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Keywords: *Click chemistry; Liquid crystals; Polymers; Elastomers;*

P-0839

ASYMMETRIC INDUCTION IN THE FREE RADICAL COPOLYMERIZATION OF ACRYLIC SUBSTITUTED AMIDE

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The chemical composition and micro organization, particularly called tacticity, are mainly determiner for final properties of materials. Very interesting aspects regard obtaining the stereoregulate structures by free radical polymerization. In this context, stereoregulation methods has been devised for the radical polymerization of several monomers including methacrylates and vinyl esters, and efficient stereoregulation has been attained for methacrylates and vinyl esters by utilizing solvent effects. Effect of monomer concentration was applied to alter the stereochemistry of methacrylate and acrylate polymerization. All these studies treat only the polymerization aspects without approach to the copolymerization process in free radical mechanism.

In this idea, the aim of this study is underline the stereochemical implication of solvent in the polymerization process of two-substituted acrylic amide (N- acryloyl-morpholyne and N-methyl-N-vinyl acetamide) recognized for theirs application in biological field.

For now, the main purpose was to investigate the effect of the solvent and temperature amongst the structure and composition of the products. Furthermore, the isotactic properties had our interest too, so we studied the same influence on the polymer tacticity.

The elemental analysis, ^{1}H NMR, ^{13}C NMR analysis allows quantitative assessment of the constituent sequences of the material.

Keywords: *Asymmetric synthesis;*

P-0840

KINETIC INVESTIGATION OF PHENYLSELENOETHERIFICATION OF SOME ?4-ALKENOLS IN PRESENCE OF CATALYTIC AMOUNT OF COCL$_2$

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The phenylselenoetherification of unsaturated alcohols is the one of the most rapid and convenient methods for formation of THF and THP type of rings. The convenient position of a double bond and a hydroxyl group in an alkenol can easily lead to formation of corresponding cyclization product. The reaction of selenium electrophiles with alkenols is a stereospecific *anti* addition where the nucleophile (pendant hydroxyl group) attacks usually at higher substituted carbon atom (Markownikoff stereoselectivity).[1] Despite the established synthetic utility of these selenofunctionalization reactions, there is no many report on a detailed kinetic investigation of these transformations.[2] In previous work it was found that in the presence and absence of various additives these reactions follow the mechanism of bimolecular nucleophile substitution S_N2 pathway.[2c]

In this work we reported the kinetic study of the cyclization of some Δ^4-alkenols with PhSeX (X=Cl, Br) in presence of catalytic amount of $CoCl_2$. We investigated the influence of olefinic and carbinol substitution pattern in some Δ^4-alkenols on the rate constants of the cyclization under the *pseudo*-first order conditions, in the presence and absence of $CoCl_2$, by UV-VIS spectrophotometry. Reactions were carried out in the THF as a solvent. The obtained values for rate constants have shown that the reactions with phenylselenenyl bromide are slower then with chloride. Reactions with $CoCl_2$ present are faster then without one. Values for rate constants strongly depend on a substitution pattern of used alkenol.

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Keywords: *Alcohols; Heterocycles; Cyclization; Kinetics;*

P-0841

2-(METHYLAMINO)PYRIDINE AS A LIGAND PRECURSOR FOR THE TI-CATALYZED HYDROAMINOALKYLATION OF ALKENES AND STYRENES

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Due to its direct and highly atom-efficient conversion of simple starting materials into more complex molecules by C–C bond formation the hydroaminoalkylation of alkenes[1, 2] and styrenes[1c, 2b] must be regarded as a very promising alternative to the industrial synthesis of amines. While reactions of 1-alkenes performed with group 5 metal catalysts (Ta, Nb) exclusively deliver the branched hydroaminoalkylation product[1] mixtures of the branched and the linear product are obtained with Ti-catalysts.[2] However, in this context, it must be noted that even with Ti-catalysts, the branched product is always formed as the major product and successful hydroaminoalkylations of styrenes can only be achieved with *N*-methyl anilines. Herein, we report the first intermolecular hydroaminoalkylation reactions of styrenes with *N*-alkyl anilines and dialkyl amines. The reactions are catalyzed by a 2-aminopyridinato Ti-complex[3] that is generated in situ from $Ti(NMe_2)_4$ and the ligand precursor 2-(methylamino)pyridine. Most importantly, it is possible for the first time to obtain the industrially more interesting linear product as the major product of the reaction.

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P-0842

METAL CATALYZED ENANTIOSELECTIVE SYNTHESIS OF ORGANIC COMPOUNDS USING FAM AND PFAM CHIRAL LIGANDS

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Asymmetric synthesis of organic compounds is an important field of ornganic chemistry. As the method, metal catalyzed asymmetric synthesis has been developed and applied by significant number of researchers worldwide for the last two decades. In this respect we have synthesized new amino alcohol based ferrocenyl aziridinyl methanol (FAM) and phosphorous based phosphino ferrocenyl aziridinyl methanol (PFAM) chiral ligands and used for metal catalyzed asymmetric synthesis of organic compounds. These ligands can be synthesized easily on a gram scale starting from acryloyl ferrocene by applying Gabriel-Cromwell reaction. Among the metal-ligand catalyzed enantioselective reactions diethylzinc addition to aldehydes was carried out to form secondary alcohols in excellent enantioselectivity. Another reaction was alkynylzinc addition to aliphatic and aromatic aldehydes which formed propargylic alcohols also in excellent enantioselectivity. In another reaction 1,3-dipolar cyloaddition of azomethine ylides was carried out to produce pyrrolidines in good yields and enantioselectivities. In the case of nitromethane addition (nitroaldol reaction) to aromatic, aliphatic, a,b-unsaturated, and heteroaromatic aldehydes and b-ketoesters corresponding b-nitroalcohols were obtained in very good yields and enantioselectivities. Diethylzinc addition to enones was also stied which formed b-ethylketones in good yields and enantioselectivities.

Synthesis of chiral ligands and their application to metal catalyzed enantioselective synthesis of organic compounds will be presented at this conference.

Keywords: *metal catalyzed asymmetric synthesis; chiral ligands;*

P-0843

NEW CHIRAL PHOSPHINE OXY AZIRIDINYL PHOSPHONATES (POAP) AS ORGANOCATALAYSTS FOR ENANTIOSELECTIVE ALLYLATION OF ALDEHYDES WITH ALLYLTRICHLOROSILANE

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New class of chiral phosphine oxy aziridinyl phosphonates (POAP-A, POAP-B, PAPA, and PAPB) were synthisized and tested as organocatalysts for the enantioselective addition of allyltrichlorosilane to aldehydes. Of the four, the chiral catalayst POAP-B showed the highest catalytic activity at ambient temparature. The enantiomeric excesses are moderate to good (up to 81 ee). In addition, temparature, solvent, equivalency and bases were screened during the optimization reactions. Dichlorometane was found to be the best solvent while diisopropyl ethylamine (DIPEA) showed highest catalytic activity as a base.

The chiral phosphine oxy aziridinyl phosphonates were prepared in 5 steps starting from diethyl vinylphosphonate with quantative yields and characterized by means of spectral analysises. Notably, the chiral aziridinyl type catalaysts were used for the first time in the enantioselective addition of allyltrichlorosilane to aldehydes. Details of this study will be presented at this conference.

Keywords: *organocatalyst; aziridinyl phosphonates; allylsilane addition;*

P-0844

SYNTHESIS OF SUBSTITUTED BIPYRIDINES AND TERPYRIDINES BY PALLADIUM-CATALYZED DIRECT C-H ARYLATION OF PYRIDINE N-OXIDES AND BIPYRIDINE N-OXIDES

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Bipyridines and terpyridines constitute an important class of heterocycles and numerous synthetic approaches have been described.[1] Cross coupling and ring assembly reactions are the most widely used. However, these synthetic routes make use of pyridyl organometallics and assembly precursor, which are frequently unstable and require multistep preparation procedures. Catalytic C-H-activation allows direct C-C-coupling and reduces the number of synthetic steps significantly.[2] In this context, we present a new versatile synthesis of functionalized bipyridines and terpyridines based on palladium-catalyzed C-H-functionalization of pyridine *N*-oxides.[3] Several examples of asymmetrically substituted 2,2'-, 2,3'- and 2,4'-bipyridine *N*-oxides, containing alkyl, methoxy, ester, nitrile, nitro, fluorine, and trifluoromethyl substituents, have been successfully synthesized. The 2,2'-bipyridine *N*-oxides have been further used for the preparation of 2,2';6',2''-terpyridine *N*-oxides, with asymmetric substitution patterns that are not easily accessible by other methodologies. The final deoxygenation of the *N*-oxides to the coressponding bipyridine or terpyridine is accomplished in high yield by either catalytic hydrogenation or reduction with PCl_3.

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Keywords: *C-H activation; Palladium; Heterocycles; C-C coupling;*

P-0845

POTASSIUM (TRIFLUOROMETHYL)TRIMETHOXYBORATE – A SHELF-STABLE TRIFLUOROMETHYLATING REAGENT

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The introduction of a CF_3 group has a profound effect on the chemical and physical properties of a molecule. This is highly beneficial in many functional molecules spanning from pharmaceuticals or agrochemicals to high performance polymeric materials.Traditional methods for trifluoromethylations operate at harsh reaction conditions and use corrosive reagents like HF, SbF_5 or SF_4. Therefore, substantial research has been devoted to the development of milder reagents suitable for a selective late-stage trifluoromethylation of functionalized molecules. State-of-the-art trifluoromethylation reactions use trifluoromethyl silanes, which are rather difficult to handle due to their volatility and moisture-sensitivity, as the sources of a CF_3 nucleophiles.

Here, we introduce potassium (trifluoromethyl)trimethoxyborate as a new source of CF_3 nucleophiles for trifluoromethylation reactions. The crystalline salt is stable on storage, easy to handle, and can be obtained in near-quantitative yields simply by mixing $B(OMe)_3$, CF_3SiMe_3, and KF. This reagent is suitable for trifluoromethylating both aryl electrophiles and nucleophiles under oxidative conditions. The scope of possible transformations includes the copper-catalyzed synthesis of trifluoromethyl (hetero)arenes from aryl iodides or boronates, and metal-free synthesis of trifluoromethyl alcohols from carbonyl compounds. Alkoxy, ester, amide, alkylamine, nitro, cyano and bromo substituents are tolerated and the reaction proceeds under very mild conditions.

This new reagent is an attractive alternative, to trifluoromethyl silanes and allows a smooth conversion of a variety of compounds into their trifluoromethyl derivatives.

Keywords: *Borates; C-C coupling; Arenes; Homogeneous catalysis; Fluorine;*

P-0846

PREPARATION OF ALPHA-SUBSTITUTED ALLYLBORONATES AND APPLICATION IN NATURAL PRODUCT SYNTHESIS

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Chiral α-substituted allylboronates are valuable tools for the stereoselective construction of homoallylic alcohols.[1,2] Diastereomerically pure allylboronates bearing (2*R*,3*R*)-1,4-dimethoxy-1,1,4,4-tetraphenyl-butane-2,3-diol as protective group for the boronic acid moiety were shown to give predominantly (*Z*)-configured allylation products in high yield and excellent enantioselectivity. For this reason these reagents are of considerable interest regarding the synthesis of natural products containing a (*Z*)-configured homoallylic alcohol moiety as a structural motif.[3]

Bench-stable α-substituted allylboronates were synthesised by [3,3]-sigmatropic rearrangements of the corresponding boron-containing allylic alcohols.[4] The extraordinary stability of the boronate moiety enabled further transformations yielding allylboronates suitably functionalised for application in envisaged syntheses of marine oxylipins. Allylic addition reactions to aldehydes furnished the desired (*Z*)-configured homoallylic alcohols in nearly enantiomerically pure form and very good yield. Furthermore, various functionalised α-substituted allylboronates were obtained by copper-mediated allylic substitution reaction of mesylated boron-containing allylic alcohols. Herein, the utilisation of organozinc halides and diorganozinc compounds allowed the introduction of side chains containing sensitive functional groups in α-position.

We will present recent progress in stereoselective synthesis of marine natural products, therein making use of diastereomerically pure functionalised α-substituted allylboronates as advanced intermediates.

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Keywords: *Asymmetric Synthesis; Natural Products; Boron; Protective Groups;*

P-0847

VISIBLE LIGHT-MEDIATED C-H FUNCTIONALIZATION USING PI-CONJUGATED ORGANIC PHOTOCATALYSTS

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Activating chemical reactions by light is a challenging task for synthetic chemists. The idea of harnessing the energy of solar radiation to enable endothermic or kinetically hindered organic reactions already arises one century ago. Besides classical photochemical transformations, the field of photoredox catalysis emerged in the last decade as a powerful tool in organic synthesis initiating organic transformations with high selectivity under mild reaction conditions. Catalyst design with respect to electrochemical and photophysical properties is crucial for the photocatalytic performance. Applied from material science different large π-conjugated organic systems frequently used as electron transport materials were synthesized and investigated as photocatalysts. The structures were selected due to favorable redox potentials, visible light absorption and chemical stability. The possibility of processing these materials as films or layers provides additional access to heterogeneous applications. Dependent on the structure the photocatalytic activity was investigated in oxidative or reductive quenching cycle. Test reaction for investigations on the oxidative quenching cycle was the photoinduced C-H arylation of unsaturated compounds with diazonium salts.[1,2] The oxidative power of the photoexcited compounds was determined by the efficiency of α-C-H functionalization of tertiary amines.[3]

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Keywords: *Photocatalysis; C-H functionalization; Cross-coupling;*

P-0848

AZOLE FUNCTIONALIZED DIACETYLENES GROUPS:SYNTHESIS, STUDIE OF THEIR POLYMERIZATION, INTERACTION WITH MOLECULES ABLE TO FORM HYDROGEN BONDING AND COMPLEXATION.

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Diacetylenes are atypical molecules due to their ability to polymerize in the solid state. This topochemical polymerization is obtained under thermal or photochemical stimulus thus leading to the formation of conjugated diacetylenic polymers. Since their discovery in 1969 by Wegner[1], polydiacetylenes have been the object of several researches. The main interests were to understand the polymerization mechanism and to study their diverse photophysical[2], optical and electronic properties[3]. Here, we will describe in the first part the synthesis of new neutral diacetylenic molecules which are functionalized by azoles groups and we will study their polymerization in the solid state[4]. Then, we will present the modification of the organization of these diacetylenes by interaction with molecules able to form hydrogen bonding and finally we will describe their use as ligands for the synthesis of Metal Organic Frameworks (MOFs).

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Keywords: *diacetylene; polydiacetylene; topochemical polymerisation; Metal Organic framewords; hydrogen bonding;*

P-0849

ENANTIOSELECTIVE SYNTHESIS OF ALPHA-CYCLOPROPYLPHOSPHONATES

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The cyclopropane ring is present in about 100 pharmaceuticals and in more 4000 naturally occurring compounds, like chrysanthemic acid in the flowers of *C. cinerariaefolium* where it has a defensive role. Some synthetic derivatives are potent pesticides. This ring is often used in medicinal chemistry to increase conformational rigidity, to increase activity of a drug or reduce its side effects, and for lead optimization. There are a few cyclopropylphosphonates with proven biological activity: insecticidal, anti-malarial, anti-viral, enzyme inhibitors and glutamate metabotropic receptor agonists. Presently chiral α-cyclopropylphosphonates are otained mainly by resolution, with chiral auxiliaries, or from chiral reagents.[1] Catalytic enantioselective methods are more efficient, since only a small amount of chiral catalyst is needed and synthetic routes are short, but examples are scarce, and usually involve transition metal-induced carbene transfer reactions with Ru, Rh or Cu complexed to chiral ligands.[2] Although very high diastereo- and enantioselectivities may be obtained, the scope is limited, since only alkyl or aryl substituents are compatible with the conditions used. As a continuation of our interests in organocatalyzed reactions applied to phosphonate chemistry,[3] we have developed an organocatalyzed method to obtain these substances with good diastereoselectivities and high enantioselectivities. The reactions proceed under mild conditions and allow for the presence of a variety of functional groups, suitable for further synthetic elaboration. Relevant results showing the scope of the new methodology and its potential for target-oriented synthesis will be presented in this comunication.

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Keywords: *asymmetric synthesis; organocatalysis; cyclopropylphosphonates; biological activity;*

P-0850

STUDIES IN THE IODINATION OF 3(5)-(2-HYDROXYPHENYL)-5(3)-STYRYL-1H--PYRAZOLES

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4-Iodopyrazoles are valuable starting materials in the synthesis of important biologically active substances. They have been used in transition-metal catalyzed cross-coupling reactions, such as Heck, Stille, Suzuki, Sonogashira and Negishi couplings and other important reactions. There are several methods reported for the iodination of pyrazoles, but they present rather complicated problems such as the use of large amounts of reactants and the lack of regioselectivity giving mixtures of iodinated compounds. So regioselective iodination of 4-pyrazolic position in order to obtain 4-functionalized derivatives is an important issue.

Continuing our work on the search for biologically active pyrazoles, now we report our findings concerning the reactivity of 3(5)-(2-hydroxyphenyl)-5(3)-styryl-1*H*-pyrazole derivatives, containing electron donor and electron withdrawing substituents in the aromatic ring of the styryl group, in the oxidative iodination using molecular iodine and ceric(IV) ammoniun nitrate (CAN) as the *in situ* oxidant. We found that the reactivity of the C-4 position in the iodination reaction is sensitive to the electronic properties of its neighboring substituents. Electron donating groups promote the monoiodination in the activated *orto* and *para* positions of the 2'-hydroxyphenyl group while electron withdrawing groups direct the iodination to the 4-position of the pyrazole ring. The structural elucidation of the obtained iodinated derivatives was accomplished by 1D and 2D NMR spectroscopic studies. Theoretical studies are underway to rationalize the obtained iodination results of 3(5)-(2-hydroxyphenyl)-5(3)-styryl--1*H*-pyrazoles.

Keywords: *Nitrogen Heterocycles; Halogenation; Iodine; Substituents effects; NMR spectroscopy;*

P-0851

DIRECT PREPARATION OF MONONITROCALIX[5]ARENE USING [4+1] CONDENSATION

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Calix[5]arene is known as an effective receptor for fullerenes C_{60} and C_{70}. Despite its excelent complexation behaviour,the utilization of calix[5]arene is limited by complicated synthesis and derivatization. The direct synthesis of calix[5]arene substituted in *p*-position significantly simplifies the process of the preparation of fullerene receptors. The commonly used methodology is a cyclization of linear dimer and trimer [2+3]. We chose another approach and optimized the cyclization of *p*-nitrosubstituted monomer and tetramer [1+4]. Surprisingly, the mass spectroscopy revealed presence of not only mononitrocalix[5]arene but also mononitrocalix[6]arene and mononitrocalix[7]arene in appreciable yield.

We studied possibilities of the separation of these higher calixarenes and the influence of reaction condition and template effect on the relative abundance of these products.

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Keywords: *calixarene;*

P-0852

SULFONAMIDE CARBAZOLES AS VERSATILE REAGENTS IN MOLECULAR RECOGNITION AND ORGANOCATALYSIS

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Carbazole is a heterocyclic compound which has been widely used as building block in the synthesis of a large number of molecules due to its synthetic versatility and optical properties. The two benzene rings of carbazole can be easily functionalized in different ways, which allows its application in different fields like molecular recognition, organocatalysis and conducting polymers.

In this work the synthesis of several 1,8-sulfonamide carbazoles is described. These compounds functionalized with hydrogen bond donors have shown excellent properties for molecular recognition and as organocatalysts.

The synthesis of the compounds is straightforward from 9*H*-carbazole, although positions 3 and 6 need to be blocked prior to sulfonation. Once 3 and 6 positions have been properly modified, sulfonation can take place simultaneously or sequentially in both positions 1 and 8. In the first case carbazole with two sulfonamide groups are easily obtained, which can be further functionalized to afford novel receptors. In the case of sequential sulfonation, the synthetic strategy provides direct access to bifunctional organocatalysts due to the introduction of different functional groups which can mimic the action mechanism of enzymes. Groups able to form H-bonds or charge transfer complexes with the substrate have been easily introduced.

These compounds have shown excellent results in several reactions with industrial interest as well as in the molecular recognition field.

Keywords: *Organocatalysis; Molecular recognition; Charge transfer; Asymmetric catalysis; Hydrogen bonds;*

P-0853

CATALYST-FREE, ONE-POT, THREE-COMPONENT STRECKER REACTION IN WATER: A SIMPLE AND EFFICIENT PROTOCOL USING ACETONE CYANOHYDRIN AS CYANIDE SOURCE

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The Strecker reaction is a milestone in organic synthesis as the classical method to obtain α-amino nitriles, important precursors for aminoacids, aminols and diamines. The classical Strecker reaction is a three-component reaction between a carbonyl compound, ammonia and an alkaline cyanide in aqueous solution, and in terms of atom-economy it represents a model.

Hydrogen cyanide is the most straightforward cyanating agent but its toxicity and volatility heavily limits widespread and practical applications in organic synthesis. To avoid the use of toxic HCN, a variety of cyanating agents were used. As an example TMSCN is widely used in the Strecker reaction, but Brönsted or Lewis acids or bases are often required as catalysts. Acetone cyanohydrin in water is frequently used in chemoenzymatic synthesis of cyanohydrines via transhydrocyanation, but surprisingly it found few applications in the Strecker reaction.

Here we illustrate a simple, convenient, and practical method for the synthesis of α-aminonitriles through a one-pot three-component Strecker reaction of a carbonyl compound, amine, and acetone cyanohydrin in water.[1] Reactions proceed very efficiently without any catalyst at room temperature with high chemoselectivity and giving in some cases the expected α-aminonitrile pure just after direct separation from water. The protocol is particularly efficient on both aliphatic or aromatic aldehydes and cyclic ketones, in combination with primary and, interestingly, with secondary amines. The asymmetric version of the protocol by using amino esters and amino alcohols coming from natural chiral pool was also developed, in particular derivatives of phenylglycine, phenylalanine, tripthophane and proline were used as chiral auxiliary leading to some unprecedented chiral α-aminonitriles and related derivatives.

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Keywords: *Multicomponent reactions; cyanides; aldehydes; ketones; amines;*

P-0854

SYNTHESIS OF NOVEL ANION RECOGNITION UNITS AND ESTIMATION OF THEIR BINDING ABILITY

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Anion receptor chemistry is a fast growing field in modern chemistry. Urea, thiourea and amide based receptors have been well studied in their ability of binding anions [1, 2, 3, 4] but there are only view studies on sulfonamide groups as anion binding sites. As the sulfon group is very electron drawing, the amide proton is more acid and expected to be a better proton donator.[5, 6]

Here, we want to present the synthesis of novel tripodal sulfonamide and thiourea anion receptors based on different benzole platforms, in order to investigate different steric influence and preorganisation of the anion affinity.

Furthermore, we present the synthesis of a mono functional sulphonamide receptor which is attached to the same platform in order to examine the influence of the numbers of binding sites on anion recognition ability. Our focus lies in the complexation of different small spherical anions fluoride, bromide, chloride and iodide, as well as the trigonal planar nitrate.

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Keywords: *Anions; Sulfonamides; Receptors;*

P-0855

IRON CATALYZED BENZYLIC OXIDATIONS

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Oxidation of benzylic carbon atoms is one of the most important synthetic transformations in organic chemistry. Besides the stoichiometric inorganic oxidants, several metal catalyzed transformations were developed and used in organic synthesis. Recently, iron proved to be an efficient, non-toxic catalyst for the oxidation in the presence of environmentally benign oxidants.[1]

Herein, we present our results on the examination of iron catalyzed methylene oxidation. We developed new and efficient conditions for the iron catalyzed benzylic oxidation of organic compounds under mild and economic aqueous conditions. The transformation utilizes easily accessible iron sources, such as $FeCl_3$ or $Fe_2(SO_4)_3$ and aqueous solution of tert-butylhydroperoxide. We established the importance of ionic surfactant, sodium dodecyl sulfate in the catalytic transformation. This additive not only ensures micellar catalytic condition for the oxidation, but generates effective iron catalyst in situ. We also demonstrated the applicability and limitations of the developed conditions through the functionalization of different molecular architectures in order to obtain important compounds bearing carbonyl functional group.

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Keywords: *Oxidation; Iron; Micelles;*

P-0856

A STEREOCONTROLLED APPROACH TOWARDS TRICYCLIC MARINE ALKALOIDS USING ENE-YNE-ENE-RRM RCM CASCADE

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Ring-rearrangement metathesis has proven to be a powerful synthetic tool for the construction of carbo- and heterocycles and has been efficiently applied to various natural product syntheses of diverse polycyclic systems. A cascade reaction with a*diastereoselective* Ene-Yne-Ene-RRM RCM as a key step has been developed for the synthesis of tricyclic indolizines.

Dienynes turned out to be challenging substrates for tandem metathesis processes, due to a lack of selectivity-controlling groups. A rational design for the desired pathway is shown within this work: a cyclic ene subunit with a triple bond in an appropriated distance for a favored RRM, and a R-group which is not diminishing the catalyst activity, for the post-RRM RCM, offer perfect reaction control and avoid undesired side pathways.

This attractive and versatile concept can be easily applied for the synthesis of several lepadiformine/ cylindricine alkaloids.

Keywords: *Alkaloids; metathesis; natural products; synthetic methods; homogeneous catalysis;*

P-0857

AMPHIPHILIC POLY(BETA-PEPTOID)S VIA RING-OPENING POLYMERISATION (ROP)

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Poly(β-peptoid)s (β-POIs) are a group of peptidomimetic polymers, which comprise a β-alanine backbone and a substituent at the nitrogen atom. The missing hydrogen donating ability for hydrogen bonding[1] and their proteolytic stability in comparison to peptides[2] are properties, which make them interesting for a variety of applications. Although the poly(β-peptoid)s have great potential as new polymer class in different fields of research, they are not well studied until now.

Reported routes for their preparation, like solid-phase synthesis[3] or the living alternating copolymerization of N-alkylaziridines and carbon monoxide, show limitations in the DP.[1]

Another method for the synthesis of poly(β-peptoid)s is the ring-opening polymerization (ROP) of N-substituted β-amino acid N-carboxyanhydrides (β-NNCAs). Although living nucleophilic ROP of α-NNCAs offers excellent synthetic control and can be performed in a wider range of solvents,[4] publications about the β-analogs are rare.[5, 6] Here we present a route for the synthesis of β-NNCAs and their ROP under different conditions. We are able to show for the first time that ROP of β-NNCAs has a living character.[7] Thus, complex architectures and highly defined polymers should be accessible, which is currently investigated in our lab.

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Keywords: *peptidomimetics; ring-opening polymerization; polymers; block copolymers;*

P-0858

NEW CATALYTIC HALOGENATION STRATEGIES FOR THE GENERATION OF UNUSUAL REACTIVITIES

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The halogenation of organic molecules is one of the most widespread techniques for the functionalization of substrates, which is often attributed to the good leaving group nature of halogen atoms in a multitude of substrates. Compounds bearing halogen atoms are thus versatile starting materials as well as intermediates in organic syntheses. Due to the intrinsic properties of the halogen substituents these molecules also play important roles in medicinal chemistry, material science, and as agro chemicals. Despite the broad application of halogenated compounds, common strategies for the formation of carbon-halogen bonds often suffer from severe drawbacks such as stereo- and regioselectivity issues, making the development of more selective and thus more atom economic and environmentally friendly methods a rewarding goal.

Our research therefore addresses the problem of catalytic halogenations by developing mild, generally applicable, and selective catalytic methods for the directed oxidative formation of carbon-halogen bonds. One aspect within our research program tries to unlock hidden reactivities by catalytically activating common halogenation reagents in order to access new structures under mild conditions. Our recent advances in developing novel halogenation strategies will be discussed.

Keywords: *organocatalysis; halogenation; iodine(III); natural products;*

P-0859

CHEMO-ENZYMATIC CONCEPTS FOR THE SYNTHESIS OF COMPLEX BACTERIAL NATURAL PRODUCTS

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The use of chemical entities isolated from natural sources has been of particular significance for human health. This can be rationalized by the often observed high selectivity and potency of such natural products towards a distinct target. Their chemical preparation is, however, often characterized by a high number of individual synthetic steps using seemingly superfluous protective groups, overall low chemical/optical yields, and the necessity of expensive and sometimes highly toxic reagents. Novel approaches towards the preparation of structurally complex metabolites by combining the strengths of total organic synthesis with the efficacy of nature's strategies to generate molecular complexity have the potential to solve these problems. Our research is therefore focused on understanding and applying biosynthetic enzymes as biocatalysts for the preparation of biomedically relevant natural products in efficient biomimetic ways. Recent achievements towards the chemo-enzymatic preparation of synthetically challenging bacterial non-ribosomal peptides will be discussed.

Keywords: *Natural products; biosynthesis; Biomimetic synthesis; Biocatalysis;*

P-0860

ADAPTATION OF IMINE CONSTITUENTS IN DYNAMIC COVALENT SYSTEMS UNDER REVERSIBLE PHASE SEPARATION

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The dynamic selection of interconverting imines has been achieved by the reversible separation of a homogeneous liquid phase into two non-miscible phases by the action of either a physical stimulus or by addition of a chemical effector. This results in the re-organization of a dynamic library based on the medium preference of the library members. Moreover, we demonstrate reversibility in the library re-organization by interconversion between the biphasic mixture and the homogeneous solution. Finally, we note that such processes provide access to dynamic non-equilibrium systems.

Keywords: *Exchange interactions; Molecular evolution; Schiff bases; Amines; Aldehydes;*

P-0861

CONJUGATED DONOR-ACCEPTOR-COPOLYMERS FOR POLYMER SOLAR CELLS

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One of the most-promising donor materials for polymer solar cells (bulk heterojunction solar cells with polymer/fullerene blends) are donor-acceptor copolymers. Currently, there is a quest for new materials to achieve solar cells with higher efficiencies. More and more complex building blocks are synthesized and incorporated into polymeric materials.

Another possibility for the optimization of the polymer structures is the combination of different building blocks within one polymer. Some examples, which are described in the literature, of random copolymers, which contain two or three different building blocks, showed promising performance in solar cells. They revealed higher efficiencies than both homopolymers.

In this context, we report the systematic synthesis of three different donor-acceptor-copolymer libraries, which contain two different acceptor moieties. The optical and electronic properties of these copolymer libraries were investigated in detail. The absorption of these polymers is broadened due to the presence of two different acceptor moieties within the polymers. Moreover, the emission of these materials is governed by the acceptor moiety, which features the lower energy.

The performance of the random copolymers in polymer solar cells was investigated in detail. Additionally the corresponding homopolymers and blends of two homopolymers have been studied in solar cell tests in order to investigate the influence of the copolymerization of two different acceptor moieties. Some of these copolymers featured higher efficiencies than the homopolymers and their mixtures. The influence of the polymer composition and of the combination of different acceptor moieties on the performance of random copolymers in solar cells will be discussed in detail.

Keywords: *Conducting materials; Polymers; Combinatorial chemistry; Donor-acceptor systems;*

P-0862

SYNTHESIS AND ANTIVIRAL EVALUATION OF SOME NOVEL PYRAZOLES AND PYRAZOLO[3,4-D]PYRIDAZINES BEARING THE 5,6,7,8-TETRHYDRONAPHTHALENE MOIETY

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Objective: Synthesis of new series of 5,6,7,8- tetrahydronaphthalene derivatives conjugated with pyrazole and pyrazolo[3,4-*d*]pyridazine functionalities hoping to produce antiviral activity against Adenovirus type 7 and human Rotaviruses.

Background: Literature survey showed that many derivatives bearing tetrahydronaphthalene nucleus attached to different heterocyclic functionalities exhibit wide spectra of biological activities[1, 2]. Adenovirus infections cause pneumonia and disseminated disease in both immunocompromised and nonimmunocompromised hosts and Rotaviruses are the single most important cause of severe diarrhea illness in infants and young children in both developed and developing countries worldwide.[3, 4]

Methodology: The enaminone **2** was reacted with hydrazonyl halides **3a-d** to afford the corresponding pyrazole derivatives (**6a-d**) which reacted with hydrazine hydrate to afford the new pyrazolo[3,4-*d*]pyridazine derivatives **7a-d**, respectively. In addition, compound **2** was reacted with some primary aromatic amines to give the corresponding secondary enaminones **10a-c** and reacted with sulphapyridine or sulphapyrimidine to produce the corresponding sulphonamide derivative **12a** and **12b**.

Results: Evaluation of these new compounds against rotavirus Wa strain and adenovirus type 7 showed that (**6c**, **6d**, **7c**, **7d**, **10b**, **10c**, **12a**, and **12b**) exhibited high efficiency as antiviral agents.

Conclusion: Some tested compounds of pyrazole, pyrazolo[3,4-*d*]pyridazine, secondary enaminones, and sulphonamides contributed to tetrahydronaphthalene moiety showed antiviral effect against adenovirus type 7 and human rotavirus Wa strain which may be considered as promising antiviral compounds.

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Keywords: *Enaminone; pyrazole; pyrazolo[3,4-d]pyridazine; sulphonamide; antiviral activity;*

P-0863

SYNTHESIS OF A MOLECULAR MUSCLE FOR OPERATION ON A SURFACE

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The design and synthesis of molecular mashines is one of the most active fields in synthetic and supramolecular chemistry. Attention was given to the immobilization of functional molecules on surfaces, particularly Au(111).

Among the known methods to attach functional molecules to gold, the platform concept developed by Herges et al. proved to be particularly successful. Triazatriangulenium (TATA) -ions are used as molecular platforms, which form self assembled monolayers (SAMs) on Au(111)-surfaces.[1] Molecules (e.g ethynyl or pheny) can be attached to the central carbon atom of these platforms that stand like poles with a pedestal on the surface.[2] In the present study a molecule was synthesized in which two “poles” were horizontally connected by an azobenzene (“laundry line molecule”).

The photochemical switching of the azobenzene should lead to a shortening of the distance between the platforms. The movement resembles the contraction of a muscle so that the molecule was named “molecular muscle”.

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Keywords: *molecular muscle; platform concept; gold surface;*

P-0864

A BORON CATALYZED ALDOL REACTION

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The aldol reaction plays an important role in the formation of C-C-bonds. A major challenge in the catalytic aldol reaction is selectivity, since the reaction is immediately followed by the elimination of water[1]. Boronic acid derivatives were demonstrated to be valuable catalysts for the aldol reaction; however they have to be dissolved in water[2, 3]. We developed a tetrahedral boronate salt, which is soluble in organic solvents. Therefore we are able to perform the reaction in the substrate, acetone.

The aldol reactions were performed with our soluble catalyst, sodium (3,5-difluorophenyl) triisopropoxy boronate. The Aldol reaction is carried out in a short reaction time with a good conversion for an electron poor aromatic system. After 20 min. 80 % conversion (38% aldol) was obtained with 4-Methoxybenzaldehyde. Performing the reaction with benzaldehyde gave good selectivity. After 20 min. 73 % of the aldol product and 23 % of the elimination product were obtained. An extensive screening of substrates and reaction conditions will be presented.

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Keywords: *Catalysis; Solvent free; boron;*

P-0865

PROGRESS IN THE SEARCH FOR THE C-CN$_2$ CARBENE

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Experimental evidence and computational results suggest that 3-bromodiazirine-3-carboxylic esters (1) undergo anionic fragmentation to the bromodiazirinyl anion (*c*-CN$_2$Br$^-$), a weakly bound complex of the bromide ion and diazirinylidene (*c*-CN$_2$), formally the simplest *N*-heterocyclic carbene (NHC) containing two nitrogen atoms. Esters 1 react with alkoxides to afford the corresponding carbonates via nucleophilic acyl substitution. The *c*-CN$_2$Br$^-$ leaving group dissociates to the strongly electrophilic *c*-CN$_2$ (*cf.*the classical nucleophilic NHCs), which is then transformed in the presence of an alcohol to an alkoxymethylene (ROCH) via a 3-alkoxydiazirine. The ROCH carbene inserts into the O–H bond of the alcohol resulting in an isolable product, dialkoxymethane. Additionally, 2-oxabicyclo[4.1.0]heptanes are formed from the nucleophilic ROCH by an intramolecular cycloaddition when some 4-alken-1-ols are employed. The alkoxide cleavage of 1 is always accompanied by the evolution of N$_2$. When the reactions are performed in amidic solvents, mixtures of N$_2$ and CO result (even under oxygen-free conditions). This observation can be explained by an oxygen atom transfer from the solvent to the *c*-CN$_2$ followed by fragmentation. In the gas phase, collision-induced dissociation (decarboxylation) of the 3-bromodiazirine-3-carboxylate ion generated from the ester 1 results in the appearance of a CN$_2$Br$^-$ ion. The constitution of this species remains to be determined, however, its facile loss of the bromide ion agrees well with the proposed precursor of *c*-CN$_2$.

P-0866

POLY(THIOPHENE-PHENYLENE-VINYLENE)S BY OXIDATIVE POLYMERIZATION

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Electroluminescent conjugated polymers are of great interest for the electronic industry and academia. Different π-conjugated polymers are applied in several optoelectronic devices like light-emitting diodes, solar cells and field-effect transistors[1]. They have the advantages over the inorganic semiconductors such as low cost, thin size and good flexibility[2].

Our works concern of the synthesis of various organic materials for these electronic applications. The main structures of our π-conjugated compounds are substituted phenylene-vinylene units with terminal thiophene groups. They are synthesized in a four- or seven-step sequence based on hydrochinone and thiophenecarbaldehyde. The important step in our monomer route is the *Horner-Emmons* olefination with high *(E,E)* selectivity[3]. On one hand the polymerization can be realized in solution by oxidation with*Lewis* acids like antimony(V)chloride or by *Grignard* metathesis. We can monitor the oxidative polymerization by UV absorption. On the other hand the polymerization can be performed electrochemically[3]. Homogenous polymer films were produced this way. They were analyzed inter alia by nanoindentation or AFM. Alternative polymer films will be obtainable from our soluble polymers by spin coating.

We attached various substituents like linear and branched alkyl groups, *β*-cyclodextrine, etc. to our monomers and the resulting oligomers and polymers. Some attachements were realized via Huisgen [2+3] click chemistry[4]. One of our future targets is a water soluble π-conjugated polymer.

Optical and electrochemical data of our substituted bis(thiophenyl-vinyl)-benzenes derivates demonstrate that they can be potential building blocks for optoelectronic materials.

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Keywords: *polymers; click chemistry; electrochemistry; Grignard metathesis;*

P-0867

BAMBUSURIL DERIVATIVES AND THEIR SUPRAMOLECULAR PROPERTIES

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Bambusurils are a family of macrocycles based on glycoluril with interesting supramolecular properties. They are promising receptors for a variety of anions because of their selectivity and stability of resulting complexes. Supramolecular as well as physical properties could be tuned by the modification of the bambusuril structure or by the preparation of homologues with various number of glycoluril unit within the macrocycle.

At this meeting we will demonstrate the differences in supramolecular behavior of selected bambusuril derivatives bearing various functional groups on their skeleton.

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Keywords: *Anions; Heterocycles; Macrocycles; Receptors; Supramolecular chemistry;*

P-0868

SYNTHESIS OF NEW MONOMERS FOR CONDUCTING POLYMERS

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In organic synthesis, the formation of new carbon-carbon bonds is one of the most important reactions, enabling the construction of complex molecular structures from simple building blocks. A variety of structures can be linked to each other in the most efficient way by cross-coupling reactions.[1–2]

Selective cross-coupling reactions which can distinguish between different halogens and pseudo halogens are well described and an important tool in the field of organic synthesis.[1, 3–4] Cross-coupling reactions which are selective with respect to nucleo-philes (RM) on the other hand offer great potential, but at present they are virtually unexplored.Therefore, new orthogonal metal-selective cross-coupling reactions between aromatic components were explored. The resulting compounds had both one metal and one halogen functional group. These functional groups are essential for the polymerization by a living polymerization process.

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Keywords: *Cross-coupling; Polymers; Polymerization; Transition metals;*

P-0869

DEVELOPMENT OF NEW CLICKABLE TURN-ON TYPE FLUORESCENT DYES

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The importance of fluorescence labeling-based techniques is probably best demonstrated by the continuously increasing number of publications on the topic. Low detection limits, high sensitivity, good temporal and spatial resolution and the relatively cheap detection of the fluorescence signal all contribute to the popularity of fluorescence-based methods.

Labeling of biomolecules by means of fluorescent tags is one of the most important topics within these techniques. The use of conventional fluorescent tags always requires the separation of unreacted dyes. Not only is there a need to omit this extra washing step is highly demanded in labeling schemes of biological matters, but the sensitivity is also further enhanced when so-called “turn-on” type of fluorescent tags are used. The unique nature of this fluorophore class is that it is virtually non-fluorescent in its unbound form, while it becomes highly fluorescent upon chemical ligation to its target biomolecule. Another case of turn-on type tags is presented by labels with emission maxima that are significantly shifted upon conjugation.

Upon our continuing efforts to fabricate turn-on type labels it was also demanded to incorporate such functionalities that allow the use of these fluorogenic tags in bioorthogonal labeling schemes. Besides, the prospective use of these tags in energy transfer (FRET) systems further demanded complete separation of excitation and emission bands a feature present in so-called mega-Stokes dyes. In line with all these criteria we have set forth a study where we designed and synthesized turn-on type of fluorescent tags possessing large Stokes shifts and functionalities that allow incorporation of these tags by means of bioorthogonal labeling schemes.

Keywords: *Fluorescence; Fluorescent probes; Click chemistry; Azides; Bioconjugate chemistry;*

P-0870

STEREOSELECTIVE OXIDATION OF ALCOHOLS USING TEMPO-PEPTIDE CATALYSTS

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Oxidations of alcohols to obtain ketones, aldehydes or carboxylic acids are fundamental transformations in synthetic organic chemistry. A transition metal-free aerobic alcohol oxidation with TEMPO as a catalyst is feasible and useful for organocatalysis.[1] TEMPO could be easily attached in small peptides to achieve chiral nitroxide radical derivatives. Synthesized TEMPO-peptides[2] have been tested as chiral catalysts for the oxidative desymmetrization[3] and the oxidative kinetic resolution[4] of diols.

The highest enantiomeric excesses were observed for catalysts including the rigid, cyclic amino acid TOAC (2,2,6,6-tetramethylpiperidine-1-oxyl-4-amino-4-carboxylic acid).[5] Syntheses of other peptide derivatives bearing the TEMPO function are in progress. Our goal is to include the enantioselective oxidation process in a multicatalytic system.[6]

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Keywords: *Organocatalysis; Oxidation; Peptides;*

P-0871

TANDEM MICHAEL ADDITION/RADICAL CYCLIZATIONS FOR THE CONSTRUCTION OF HIGHLY FUNCTIONALIZED CYCLOPENTANES

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Tandem reactions are an effective tool in synthetic organic chemistry, since they allow the time- and resource-efficient access to complex structures from simple precursors.[1]

The methodology employs a diastereoselective Michael addition, where enolates of different carbonyl compound classes are successfully coupled with various Michael acceptors. The diasteroselectivity of the Michael addition can be switched using either Z- or E-enolates of esters.[2] This is pivotal steering element that controls diastereoselectivity of the subsequent radical cyclization. Those two aspects allowed to construct highly functionalized cyclopentanes diastereoselectively in a one pot procedure. The interconversion between anionic and radical stage is mediated either by ferrocenium hexafluorophosphate, a recyclable, less toxic single electron transfer oxidant or by 2,2,6,6--tetramethyl-1-oxopiperidin-1-ium hexafluorophosphate, which enables catalytic tandem processes. The whole sequence is terminated by trapping with the TEMPO radical.

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Keywords: *Cyclization; Diastereoselectivity; Michael addition; Radical reactions; Domino reactions;*

P-0872

A HIGHLY CONVERGENT ROUTE TOWARDS 4-AMINO-4-DEOXY-L-ARABINOSE MODIFIED LIPID A

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Lipid A of gram negative bacteria anchors the lipopolysaccharide chain to the outer cell membrane. It possess a rather conservered structure: To a β(1-6) diglucosamine backbone are phosphates attached at positions 1 and 4'. Different acylation pattern are possible for positions 2-N, 2'-N, 3, 3', were (*R*)-3-hydroxy or (*R*)-3-acyloxy fatty acids could be attached.

Covalent modification of Lipid A by cationic β-L-Ara4N at either both 1- and 4'- phosphates or solely at the reducing phosphate, which is characteristic for *Burkholderia* strains, is associated with augmented bacterial virulence, resistance to antibiotic treatment and modulation of TLR4-MD-2-mediated innate immune response. Mono- and bis- β-L-Ara4N substituted Lipid A structures, corresponding to native *Burkholderia* Lipid A were synthesised.

Starting from glucosamine, an orthogonally protected Glc2N key intermediate was assembled, carrying 2-*N*-Troc-, 1-*O*-TBDMS- and 4,6-*O*-anisyliden protecting groups, position 3 was acylated with (*R*)-3-(((allyloxy)car-bonyl)oxy)tetradecanoic acid. The compound was used for the synthesis of a glycosyl donor by regioselective reductive opening of 4,6-O-anisylidene acetal to furnisch 4-OPMB ether, followed by 6-*O*-Alloc protection, 1-*O*-desilylation and subsequent appel reaction to give a bromide donor. Glycosyl acceptor was prepared in a convergent manner using the same precursor by acetal opening to provide 6-*O*-PMB ether, 4-*O*-Alloc protection, cleavage of 2*N*-Troc group followed by acylation with 3-oxyacyl lipid chain. Subsequent 6-*O*-PMB deprotection and glycosylation of the liberated 6-OH by bromide donor, reductive cleavage of 2'-*N*-Troc protection and *N*-acylation afforded fully protected pentaacylated β(1-6) diglucosamine disaccharide. Regioselective deprotection of positions 4'-*O*-PMB and 1-*O*-TBMS allowed for selective coupling with either diallyl-*N,N*-diisopropylphosphoramidite or H-phosphonate of 2,3-di-*O*-Alloc-protected β-L-4-azido--arabinose, respectively, leading, after global deprotection (Alloc deprotection followed by azide reduction), to target *Burkholderia* Lipid A structures.

Keywords: *Synthetic methods; Carbohydrates; Phosphorylation; Phospholipids; Azides;*

P-0873

UNUSUAL BEHAVIOUR OF 5-(2-PYRIDYL)SULFINYL-TETRAPROPOXY-CALIX[4]ARENE IN PD-CATALYZED REACTION.

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Palladium catalyzed cross-coupling reactions using direct C-H bond activation is very attractive topic in modern synthetic organic chemistry. The presence of a directing group usually enables regioselective introduction of the coupling agent into a specific position. Among these groups, the 2-pyridylsulfinyl moiety possesses very strong C-H activating properties. We have introduced this directing group into the upper rim of calix[4]arene and attempted the direct arylation of calixarene skeleton into the meta position. This reaction should provide very interesting inherently chiral systems which could be useful in the design of novel chiral receptors. Surprisingly, we have found that the isolated product is not the expected aryl-substituted calixarene, but some unknown, meta substituted and inherently chiral calix[4]arene derivative. The NMR spectra of this compound were very complicated and did not lead to the structure elucidation. On the other hand, the single-crystal X-ray crystallography gave us the final solution. The activation of the neighbour C-H bond (next to the 2-pyridylsulfinyl directing group) led to the unexpected intramolecular bridging of two *meta* positions on the proximal phenolic subunits via a direct C-C bond. This kind of reaction has never been observed in calixarene chemistry. The application of this phenomenon for the synthesis of inherently chiral calixarene-based receptors is currently underway.

Keywords: *Calix[4]arene;*

P-0874

SYNTHESIS OF NOVEL ENE-YNE COMPOUNDS DERIVED FROM SELENIUM HETEROCYCLES

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Organoselenium compounds have become attractive synthetic targets in material synthesis, ligand chemistry and biologically relevant processes. Among organoselenium compounds, selenophene derivatives are widely studied because of their potential application in organic electronics.[1] Despite structural similarities, however, sulfur and selenium compounds are often strikingly different with respect to their stability, properties, and ease of formation.

The topic of this contribution will be the presentation of organoselenium-based functional organic materials. On the one hand the structural focus will be on novel annealed selenophene scaffolds; on the other hand an investigation of selenophene ring-opening moieties towards ene-yne compounds will be presented. Based on various 2-bromoselenophene derivatives, bearing different substituents (H, alkyl, aryl) in α- respectively β-position, the Halogen-Dance (HD) reaction[2] proves to be a versatile synthetic route to multisubstituted selenophenes. Subsequent controlled selenophene ring fragmentation reaction selectively leads to the Z-isomer of ene-yne compounds. Further modification by microwave-assisted Cu-catalyzed Huisgen cycloaddition[3, 4] affords the corresponding triazoles as 1,4-adducts. The applicability of these triazoles in organic electronics will be discussed.

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Keywords: *Organic Electronics; Selenophene; Selenophene Ring Fragmentation; Halogen Dance Reaction; Huisgen cycloaddition;*

P-0875

DIRECT COUPLING OF COX WITH EPOXIDES: CATALYTIC PRODUCTION OF BIODEGRADABLE POLYMERS

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The development of catalysts for activation and use of carbon oxides (CO and CO_2) as a feed-stock for synthesis of new materials is an attractive research target in last 20 years. One of the most promising strategies of carbon oxides utilization is direct coupling/copolymerization of CO and CO_2 with epoxides. Depending on catalytic system (catalyst/cocatalyst ratio) and experimental conditions either cyclic esters/carbonates or polymers susceptible towards biological or hydrolytical degradation can be obtained.

The aim of this work is to develop effective catalytic system for direct conversion of carbon monoxide and carbon dioxide and epoxides to biodegradable polymers or to their cyclic esters precursors, which can be easily polymerized via metal-catalyzed ring-opening polymerization. For this purpose chromium and cobalt SALEN complexes were synthesized and tested as catalysts for direct high-pressure epoxide/CO_2 copolymerization. The effect of cocatalyst and experimental conditions (temperature, pressure of CO_x and epoxide/catalyst/cocatalyst ratio) was also investigated. Similar catalytic complexes (combination of SALEN complexes with $Co(CO)_4$ salt) were also tested for direct coupling of epoxides with CO.

Keywords: *Polymerization; Chromium; Cobalt; Carbonylation; Carbon dioxide fixation;*

P-0876

NOVEL APPROACH TO SYNTHESIS OF CALIX[4]ARENE RECEPTORS

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Calix[4]arenes are widely used as platforms for synthesis of receptors acting in host-guest chemistry. The structure of calixarene molecule allows interactions with all types of substrates (soft or hard metal cations, anions and even neutral molecules).[1] Due to various shapes of anions and their solvent-dependent stability, the most sophisticated design is required for their effective binding.[2]

In this research, a novel regioselective derivatisation[3] of calix[4]arene skeleton has been developed and optimized. This multi-step synthetic procedure leads to interesting derivatives with so far almost inaccessible substitution pattern. A subsequent modification enables to prepare precursors for ureido-based anion receptors fixed in a *cone* and a *partial cone* conformation, and for versatile receptors which adopt a *1,2-alternate* conformation. Some of them have been synthesized and used for the complexation experiment. The results as well as the synthetic approach will be presented.

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Keywords: *calix[4]arenes; host-guest chemistry;*

P-0877

STEROID PROBES FOR THE STUDY OF TRANSPORT IN A LIVING OBJECTS

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Steroids and steroid-like compounds are important molecules for many living organisms. They act as a building blocks of membranes, take part in the digestion, and in the signaling pathways. Although many of the steroid roles have been already understood; a lot of them are continuously being explored. One example of new and attractive avenues of investigation is the research of the synthesis and action of neurosteroids in the brain. Recent development in the methodologies of the biological processes allows revealing roles of neurosteroids more straightforward. However, these new methods demand effective molecular standards and probes.

We have prepared steroid molecules labeled with isotopes, fluorescent, or photoactive moieties. These probes were used for the assessment of pharmacokinetics of steroidal neuroprotectives and for the study of their transport to the neurons.

Keywords: *steroids; isotopic labeling; fluorescent probes;*

P-0878

TOWARDS THE SYNTHESIS OF APICULAREN A: AN APPLICATION OF NEW METHODOLOGY TO CONSTRUCT 2,6-ANTI-TETRAHYDROPYRAN RINGS

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Since the isolation[1] and the subsequent structural elucidation[2] of Apicularen A, **1**, by Hofle and co-workers, the molecule has been an intriguing molecule to the chemical society. Its wondrous biological properties[3] place Apicularen A as a potential candidate for anticancer drug target and the delicate architecture of the molecule are two major factors that motivate many synthetic chemists to construct Apicularen A. The first total synthesis successfully reported by De Brabander and co-workers[4] and there are hitherto 11 total syntheses and numerous formal syntheses for this interesting molecule found in the literature. Our group also became interested and jumped onto the bandwagon in the attempt to construct the molecule. We embarked on our synthetic study with commercially available 2,6-dihydroxybenzoic acid and effected a hetero-Diels-Alder to obtain intermediate **2**. We then applied a new methodology recently developed in our group,[5] which involves Mukaiyama-Michael addition of silyl enol ether that is catalyzed by indium trichloride ($InCl_3$), to dihydropyranone at ambient temperature to yield the desired, 2,6-*anti*-tetrahydropyran intermediate **3** with high diastereoselectivity.In conclusion, we managed to demonstrate the applicability of the methodology developed and the total synthesis of Apicularen A is currently still underway.

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Keywords: *Synthetic methods; Total synthesis; Michael addition; Indium;*

P-0879

SYNTHETIC AND MECHANISTIC STUDIES ON NICKEL-CATALYZED C–C BOND FORMATIONS APPLYING WELL-DEFINED NICKEL COMPLEXES MODIFIED BY TRIDENTATE O,N,O'-LIGANDS

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Nowadays nickel-catalyzed carbon–carbon bond formations have been extensively developed, and have been used in synthesis of fine chemicals and natural products. In contrast to well established sp^2–sp^2 cross coupling reactions, sp^3–sp^3 cross coupling reactions are more challenging tasks, because of the several problems, e.g., β–hydride elimination.[1] One option to overcome these problems is the design and fine-tuning of the catalyst, which has been demonstrated in a number of studies. Nevertheless, the development of novel ligands is still requested for improving the catalyst performance. Furthermore the understanding of the underlying reaction mechanism is also important to advance these reactions.

Recently we studied the abilities of octahedral nickel complexes containing O,N,O?–ligands in coordination chemistry and catalysis.[2] Moreover, the octahedral nickel complexes were successfully applied as pre-catalyst in cross coupling reactions. Hence, we report herein the synthesis and characterization of square planar nickel complexes modified by tridentate O,N,O?–ligands and a phosphane as an additional ligand, which can be a useful probe (e.g., NMR). Moreover, the capability of the complexes were investigated in C(sp^2)–C(sp^3) cross coupling reactions of aryl halides with zinc reagents and experiments to shed light on the underlying reaction mechanism were performed.

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Keywords: *Homogeneous catalysis; C-C coupling; Nickel; Tridentate ligands; Reaction mechanisms;*

P-0880

POLY(CARBOSILAZANE-B-STYRENE) – NOVEL HYBRID BLOCK COPOLYMERS VIA SEQUENTIAL ANIONIC POLYMERIZATION

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Novel hybrid diblock copolymers of the type poly(carbosilazane-*b*-styrene) were synthesized via sequential anionic polymerization. N-trimethylsilyl-1,1,3,3-tetramethyl-1,3-divinyldisilazane was polymerized in n-hexane using butyl lithium as initiator[1]. As obtained living polycarbosilazane chains were subsequently used as macroinitiators for the anionic polymerization of styrene in a mixture of n-hexane and toluene (1:1). Standard methods (IR, NMR, size exclusion chromatography (SEC)) were applied for the characterization of the obtained polymers. Absolute molecular weights were obtained by analysis of SEC eluents with an additional light scattering detector. The Flory-Huggins interaction parameter, χ, for the block copolymer system was calculated[2] from related homopolymer solubility parameters in order to make a theoretical prediction of the block copolymer microphase behavior. Polymer films were prepared from a variety of solvents and analyzed by microscopic methods (scanning electron microscopy, transmission electron microscopy, atomic force microscopy). Finally, the accuracy of theoretical predictions was assessed by comparison with experimental findings.

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Keywords: *Block copolymers; organic-inorganic hybrid composites; self-assembly; solvent effects;*

P-0881

PREPARATION OF BIODEGRADABLE POLY(LACTIC ACID-CO-GLYCOLIC ACID) BY LIPASE CATALYZED COPOLYMERIZATION PROCESSES

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Poly(lactic acid-co-glycolic acid) was obtained by lipase catalyzed copolymerization of L-lactic acid and glycolic acid. The structure of poly(lactic acid-co-glycolic acid) was characterized by IR, ^{1}H NMR and MALDI-TOF spectrometry. The influence of the reaction conditions, such as solvent, temperature and the type of lipase was studied to optimize the synthetic procedure. Low molecular weight copolymers can be produced from lactic acid and glycolic acid by using enzyme lipase B from Candida Antarctica (Novozyme 435) at 50 °C in a 5-hour reaction.

Keywords: *biopolymers; enzymatic polymerization;*

P-0882

SELECTIVE CONVERSION OF KETONES INTO HYDROPEROXIDES: FROM CRIEGEE INTERMEDIATE TO ANTIMALARIAL TETRAOXANES

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One of the most famous conversion of ketones into hydroperoxide was found during the investigation of Baeyer-Villiger oxidation, where Criegee intermediate was postulated as an intermediate, although this intermediate in reactions with hydrogen peroxide was elusive.[1] Recent developments in the preparation of α-heteroatom substituted hydroperoxides (*gem*-dihydroperoxides...) are interesting due to their diverse bioactivity.[2] Furthermore they are synthetic intermediates for the preparation of various cyclic peroxides via cyclization reactions. The most notable example is antimalarial activity of cyclic peroxides that are active against the chloroquine resistant strains of malarial parasites.[3]

The most general method for hydroperoxides is the ozonolysis of ketone enol ethers or a-olefins in the presence of either H_2O_2 or alcohol, while alternative methods include acid-catalyzed peroxidation of ketones or ketals with H_2O_2 reaction. The drawbacks of these peroxidations include the need for the prior synthesis of the starting substrates, the use of highly concentrated H_2O_2, the need for excess acid, moderate yields and a restricted substrate range. Neutral conditions offers a solution, however reactivity of $H_2O_2$is weak – activation with $MeReO_3$ in fluorinated alcohols or with iodine.[4]

We will present a study on the activation of peroxidation of carbonyl compounds by H_2O_2 without any catalyst, where activation of reaction occurs at the border between homogenous solution and the solvent-free reaction. Furthermore, conditions that enables selective mono- or di-hydroperoxidation were studied. The relevance of this reaction for the formation of cyclic peroxides, as well as connection with Baeyer-Villager oxidation will be discussed.

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Keywords: *Peroxides; Green chemistry; Ketones; O-O activation; Solvent effects;*

P-0883

DIHALOIODATES(I): SYNTHESIS WITH HYDROGEN PEROXIDE AND HALOGENATING ACTIVITY

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In organoiodine molecules iodine can be found in different oxidation states and forms. Most common are iodine (I) compounds, however, iodine is also capable to form stable hypervalent compounds, usually as iodine(III) and iodine(V) species.[1] Iodine(I) compounds differ in chemistry to iodine(III) and (V) compounds and serve mainly as electrophylic iodinating reagents (NIS, IPy_2BF_4, ICl).

Dichloroiodates(I) are less known analogues, although they were used for iodination of aromatics, alkenes, enaminones and flavones. Structural analogues of dichloroiodates(I) are dibromoiodates(I) and difluoroiodates(I). There is little known on chemistry of dihaloiodates(I). According to the literature, dichloroiodates(I) are prepared using strong and dangerous oxidants *i.e.* ICl, Cl_2 or hypochlorite.[2] Due to our interest on the use of "green" oxidants for oxidative halogenation,[3] we will present a study on the use of hydrogen peroxide for oxidation of iodine into iodine(I) compounds (IX_2^- salts) with an emphasis on a solvent-free method for the preparation of dihaloiodates(I) using different forms of hydrogen peroxide for oxidation of iodine in the presence of halide ions. In addition, a study on the activity of tetraalkylammonium and pyridinium dichloroiodates(I) ($Alk_4N^+ICl_2^-$) and dibromoiodates(I) ($Alk_4N^+IBr_2^-$) as halogenating reagents will be presented.

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Keywords: *Halogenation; Iodine; Hypervalent compounds; Green chemistry; Oxidation;*

P-0884

NEW CATALYTIC OXIDATIVE AND THERMAL RADICAL CYCLIZATION APPROACHES

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For some time we have been working on oxidative tandem approaches combining polar organometallic processes with radical reactions. So far these reactions had to be performed using stoichiometric amounts of ferrocenium hexafluorophosphate.[1] Here we present the first approaches to perform these tandem reactions catalytically in the metal oxidant.

Reactivity limitations of certain substrates in electron transfer-induced cyclizations are overcome by performing stoichiometric or catalytic oxygenations using TEMPO. The resulting alkoxyamines can be transformed subsequently to complex ring systems using thermal radical cyclizations employing the persistent radical effect.[2]

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Keywords: *Radical reactions; Electron transfer; Cyclization; Domino reactions;*

P-0885

PYRAZINAMIDE DERIVATIVES MICROWAVE SYNTHESIS AND THEIR BIOLOGICAL EVALUATION

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According to WHO, the number of new tuberculosis cases is falling slowly during last years. But new problems have appeared with *Mycobacterium tuberculosis* strains which are becoming more resistant to standard treatment (first line drugs as well as second line drugs), and with HIV co-infection, which leads to quicker spreading of the TBC infection. These complications have become an epidemiological problem all over the world[1].

Pyrazinamide, which belongs to the first line antituberculotic drugs, is very applicable for chemical modification and becomes a template for compounds being prepared in this research project.

3-chloropyrazine-2-carboxamide was chosen as a starting structure and was treated with a various group of aromatic amines (using a microwave reactor with focused field). This reaction yielded N-substituted 3-aminopyrazine-2-carboxamides.

Prepared compounds were purified using flash chromatography and then were chemically characterized by melting points, IR and NMR spectra, logP, logK and elemental analysis.

Biological tests *in vitro* were made afterwards. It means antimycobacterial screening (various *Mycobacterium* strains, using pyrazinamide and isoniazide as standard), antibacterial and antifungal screening (8 bacterial and 8 fungal stems, making use of neomycin, bacitracin, penicillin G, ciprofloxacine, phenoxymethyl penicillin, amphotericin B, voriconazole, nystatin, and fluconazole as standards) and testing for herbicidal activity (inhibition of the photosynthetic electron transport in spinach chloroplasts with DCMU (Diurone®) as a standard – IC_{50}).

A small group of prepared substances has shown herbicidal activity, but it has not reached as good activity as standard (IC_{50} for DCMU is 1.9 μmol/l).

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Keywords: *Pyrazinamide; Tuberculosis; Microwave; Mycobacterium;*

P-0886

SYNTHESIS AND EVALUATION OF NOVEL FLEXIBLE AND PARTLY CONSTRAINED LONG-CHAIN ARYLPIPERAZINE DERIVATIVES OF SALICYLAMIDE AS SEROTONIN RECEPTORS LIGANDS

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Continuing our previous research concerning structure-activity relationship of serotonin receptor ligands representing the long-chain arylpiperazines, novel series of ligands was synthesized. Our present study concentrated on the influence of linker conformation on the *in vitro* activity in the group of synthesized ligands. Structural modifications involved replacement of the pentyl and hexyl chain by m-xylene and p-xylene moieties, while maintaining *O*-substituted salicylamide and 2-methoxyphenylpiperazine motifs on both sides of the modified linker. To check the impact of the modifications on the desired pharmacokinetic and pharmacodynamic properties of those putative CNS ligands, analysis of their physicochemical and structural properties (e.g. Lipinski's Rule of Five) and probability prediction of psychotropic activity by PASS (Prediction of Activity Spectra for Substances) was performed. Binding affinity for serotonin 5-HT$_{1A}$ and 5-HT$_7$ receptors was tested for all the synthesized compounds and was also compared with their affinity for dopamine D$_2$ receptors. The potentially bioactive conformation was investigated for the chosen ligand by means of molecular modeling techniques. To this end, we selected the most preferred conformations by docking the ligands to the binding sites of homology models of the receptors of interest. On the basis of the results of our structure-activity research, new lead structures were identified providing guidelines for further pharmacological investigation.

Keywords: *Ligand design; Synthesis design; Molecular modeling; Amides; Drug design;*

P-0887

DINUCLEAR TITANIUM COMPLEXES WITH SULFAMIDE LIGANDS AS CATALYSTS FOR HYDROAMINOALKYLATION AND HYDROAMINATION REACTIONS

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The hydroamination[1] as well as the hydroaminoalkylation[2] of alkenes must be regarded as environmentally friendly and ecologically desirable processes. For both reactions, group-IV-metal complexes have been found to be good catalysts but all of them are more or less limited in scope. For that reason, much effort has been spent on the identification of new kinds of catalysts that allow the efficient addition of *N-H* or N-*C-H* bonds across C-C double bonds. In search of new ligands for Ti-catalyzed hydroaminoalkylation and hydroamination reactions we recently focused our work on *bis*-sulfamide compounds like $O_2S(NHR)_2$. A promising synthetic approach towards this class of ligand precursors was provided by a work from Boncella *et al.*[3] who introduced *bis*-sulfamides as precursors for chelating diamide ligands for the synthesis of tantalum complexes like $Ta(NMe_2)_3[O_2S(N\text{-}tert\text{-}Bu)_2]$. Herein, we describe the first synthesis of a dinuclear Ti-sulfamido complex and its application as a catalyst in hydroaminoalkylation and hydroamination reactions. In the presence of the catalyst $[Ti(NMe_2)_3]_2[O_2S(NPh)_2]$, various aminoalkenes are converted into the corresponding hydroamination products in excellent yields while hydroaminoalkylation reactions of alkenes with *N*-methylamines give the desired products only in poor to good yields.

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Keywords: *Hydroamination; Hydroaminoalkylation; Sulfamide-Ligands; Titanium-catalyzed;*

P-0889

PALLADIUM FUNCTIONALISED MICROSPHERES FOR INTRACELLULAR CHEMISTRY

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Polymeric styrene microspheres have a great potential at the interface of chemistry, biology and medicine. Microspheres have previously been used in both cellular labelling and intracellular delivery of biomaterials.[1, 2] The use of palladium nanoparticles entrapped within cross-linked resin beads have been shown to operate in a truly heterogeneous catalysis manner.[3]

In this study the combination of these technologies produced a catalyst shown to be both non-cytotoxic and rapidly taken up by cells. This provides the basis for the customisation of a heterogeneous unnatural catalyst as a tool to carry out chemistry never known before inside a cell. The studied reactions include a Suzuki-Miyaura cross-coupling reaction for the in situ generation of a mitochondria-localized fluorophore. This opens up a wide range of possible applications ranging from cellular labelling to in cellulo synthesis and specific activation of drugs at specific targets and inhibitors of cell function.[4]

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Keywords: *palladium; cell delivery; Fluorescent probes;*

P-0890

POLYMORPHISM OF SUCCINOBUCOL AND ITS CONJUGATION WITH STEROIDS TO ALTER ITS DRUG EFFECT AND BIOAVAILABILITY

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Succinobucol, **1**, was developed as a drug for treatment of atherosclerosis. Later, its range of activity was extended on diseases induced by oxidative and inflammatory stress with focus on type 2 diabetes. Nevertheless, clinical studies on the drug showed mixed results which later lead to the failure of the drug in the approval process. Knowing some of the drug's weak points, as low ability to decrease the blood level of cholesterol and low bioavailability, we have designed a novel type of plant steroid / **1** co-drug with the goal to alter its pharmacological profile. Plant steroids or their esters are clinically used as agents lowering blood level of cholesterol and are known to also have anti-inflammatory properties. Prepared conjugates were fully characterized on their molecular and submolecular level,[1] preliminarily tested on their toxicity, bioavailability and antioxidant activity and based on the results were found to be interesting compounds for further studies of their biological activity.[2] Furthermore, four different polymorphs and one phase mixture of two polymorphs of **1** were characterized by spectral and thermoanalytical methods, and a coarse estimate of their thermodynamic stability was deduced based on the analysis of fresh and aged polymorph samples.[3] We still believe that succinobucol possesses some undiscovered potential as drug and therefore further research is desirable.

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Keywords: *Steroids; Antioxidants; Drug Design; Polymorphism; Crystal Growth;*

P-0891

WATER-SOLUBLE FUNCTIONAL PORPHYRINS AND PORPHYCENES

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Porphyrins are Nature's prime choice for electron and energy transfer purposes. To do this job properly, the dyes have to be embedded in matrices that allow for hierarchical order. Often, this ordering generates a redox gradient which increases the efficiency of electron transfer processes. Using highly charged synthetic porphyrins and dyes, it is possible to build layer-by-layer devices in water with alternatingly charged molecules with such a gradient. Water as solvent also offers the advantage of strong hydrophobic effects such as π-π-stacking for another way to order the dyes. Here, we present some of our recent results [1, 2] in this field including syntheses of novel functional water-soluble porphyrins and porphycenes.

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P-0892

MODULAR SYNTHESIS AND CATALYTIC APPLICATIONS OF P-CHIRAL PN-, PNN- AND PNNP-PHOSPHINE LIGANDS

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Chiral phosphorous-containing ligands are useful tools in organometallic chemistry as they have the capability to interact with a wide variety of transition metals and can be tailored to provide the desired electronic and steric properties. The most common residency of chirality in such compounds is on the surrounding carbon framework. However, recently P-chirogenic phosphines have garnered increased attention as means to prepare them have improved. Among such P-chirogenic phosphines, mixed PN-type ligands have shown promise in catalysis. We here present methodology that provides ready access to different P-chirogenic PN, PNN and PNNP-phosphine boranes via a modular synthesis with the possibility of varying both the steric and electronic properties of the ligands. Applications in ruthenium catalyzed hydrogenation are also presented.

Keywords: *asymmetric synthesis; phosphane ligands; chirality; ruthenium; hydrogenation;*

P-0893

NOVEL HYPER AND HIGHLYBRANCHED POLY(URETHANE-TRIAZOLE)S

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Dendrimers with their unique molecular architecture and performances have attracted considerable interests, but processes of their synthesis are usually too complicated. Hyperbranched polymers (HBP) have similar structure and performances as well as dendrimers, but unlike the latter they could be synthesized easier. This circumstance is promoted to the development of methods of the synthesis of HBP with new combinations of functional groups.

Earlier we have elaborated an approach to the synthesis of new urethane-triazole polymers with classic hyperbranched structure. It is implemented through two quantitative reaction viz. urethane formation and 1,3-dipolar cycloaddition azides and alkynes (1,3-DCA). This method consists of three stages. The first one is the synthesis of diazidourethaneisocyanate precursor via interaction between diazidopropan-2-ol (DAPOL) with an excess of diisocyanate to ensure a higher yield. Unreacted diisocyanate is separated from the precursor. On the second stage diazidoacetylene monomer is obtained by a reaction of a precursor with propargyl alcohol, and the third step is one pot synthesis of HBP. In such a way purification of monomer can be avoided.

Inasmuch as synthesis of urethane-triazole HBP is complicated because of precursor purification, it is easier to synthesize partially cross-linked highlybranched polymers (HP) which are similar in their properties to HBP. Urethane-triazol HP was obtained by 1,3-DCA from A_2+B_4 monomers without extra purification, with diurethanediacetylene as A_2 and tetraazidodiurethane as B_4. The ratio of azide and acetylene groups was varied from 2 to 3.

All synthesized polymers were characterized by ^{1}H-NMR, IR, DSC and SEC. The obtained urethane-triazol HBP and HP are yellow solids soluble in polar aprotic solvents. Owing to high adhesion to various materials they can be used as addition to coatings. Moreover a large number of terminal azide groups allow further modification of urethane-triazol HBP and HP; in particular, water soluble polymers can be produced.

Keywords: *hyperbranched polymers; highlybranched polymers; urethane formation; 1,3-dipolar cycloaddition; urethane-triazole;*

P-0894

MAGNETICALLY RECOVERABLE CUFE$_2$O$_4$ NANOPARTICLES: A CATALYST FOR THE SYNTHESIS OF ARYL AZIDES AND 1,4-DIARYL 1,2,3-TRIAZOLES FROM BORONIC ACIDS

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In recent years, application of magnetic nanoparticles has attracted great attention in many different disciplines. Besides their use in the fields of magnetic fluids, biotechnology/biomedicine, magnetic resonance imaging, data storage and environmental remediation they are widely used as catalysts for organic transformations. Due to their magnetic properties they can be easily separated from the reaction mixture by applying a magnetic field. This is a practical and efficient alternative to filtration or centrifugation as it speeds up the isolation and prevents loss of catalyst.

There are only few literature precedents on 1-aryl-1,2,3-triazoles synthesis using aryl halides, sodium azide, and terminal alkynes. These protocols use long reaction times at elevated temperature and inert gas atmosphere because of the slow azidonation of aryl halides.[1] To overcome these drawbacks, Liu *et al.* developed a copper catalyzed one-pot synthesis of 1-aryl-1,2,3-triazoles from boronic acids in order to replace the aryl halides as starting materials.[2]

To broaden the scope of magnetite based nanoparticles as robust and readily available heterogeneous catalyst with high surface area, we report a simple, efficient and sustainable procedure for the synthesis of aryl azides and a one-pot synthesis of 1-aryl-1,2,3-triazoles using CuFe$_2$O$_4$ as magnetically easily recyclable catalyst. Notably, the reaction is performed under green conditions in water at room temperature affording the desired products in good to excellent yields. Convenient magnetic separation of the catalyst eliminates catalyst filtration after completion of the reaction. The high catalytic efficiency of the nanoparticles remained unaltered even after five consecutive cycles.

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Keywords: *Magnetic Nanoparticles; Nanoparticles; Triazoles; Aryl azides;*

P-0895

SYNTHESIS OF LATE-TRANSITION METAL CATALYST TETHERED ON SILICAAND ITS L-LACTIDE POLYMERIZATION

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Plastics are used almost everywhere in the world and more environment-friendly plastics are requested from many application areas. Polylactide(PLA) is a biodegradable aliphatic polyester synthesized from renewable resources, such as corn or potato starch. PLA can be prepared by condensation of lactic acid and by the ring-opening polymerization(ROP) of the lactide. ROP is known to produce PLA with high-molecular weights. Many catalysts have been investigated for the polymerization of lactide including complexes of aluminum, zinc, tin. In this study, we constructed late-transition metal catalysts on the surface of nanoporous silica, and examined their performance in L-lactide polymerization. The resulting PLLA were characterized by FT-IR, DSC and GPC.

Keywords: *L-lactide; Polymerization; Late-transition metal; Nanoporous material;*

P-0896

VISIBLE LIGHT PHOTOREDOX CATALYSIS AS A VERSATILE TOOL FOR CROSS DEHYDROGENATIVE COUPLING REACTIONS

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In recent years, the application of visible light as a ubiquitous and renewable source of energy has attracted the interest of synthetic organic chemists. While photochemical reactions often need to be performed with high-energy UV light, the use of sunlight renders photochemical transformations highly attractive.[1]

Inorganic metal poly-bipyridyl complexes possess well-known properties and emerged as a highly potent class of catalysts for photochemical transformations. In particular, the photoexcited states of ruthenium and iridium based polybipyridyl complexes were shown to be highly efficient for catalytic oxidations of tertiary amines.[2]

Herein, we wish to present our latest findings on the photochemical oxidation of amines that can be efficiently coupled with further consecutive transformations for the efficient construction of C-C, C-P and C-N bonds. Further applications concentrated on the development of efficient dual catalytic transformations, relying on photochemical oxidations and catalytic C-C bond forming reactions for the convenient construction of functionalized amines.[3]

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Keywords: *Photocatalysis; Organocatalysis; Cross Dehydrogenative Coupling; Visible Light;*

P-0897

C3V-SYMMETRIC TETRAAMMONIUMTRIPTYCENE DERIVATIVES AS VERSATILE SYNTHETIC BUILDING BLOCK – TOWARDS GIANT SHAPE-PERSISTENT MACROCYCLES AND CAGE COMPOUNDS

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Aminotriptycenes are versatile precursor for the synthesis of shape-persistent molecules. For instant, triaminotriptycene is used for the synthesis of discrete organic cage compounds[1], whereas the hexaaminotriptycene was used to form molecular crystals with extrinsic[2] and triptycene-based metal salphens with intrinsic[3] porosities. Beside the synthesis of cyclododeciptycene quinone by Hua et al.[4], MacLachlan et al.[5] proposed a triptycene based macrocycle formed by multifold imine condensation reaction. However the macrocycle was synthetically not realized yet.

With regard to the suggested macrocycle[5] we developed a versatile route for the synthesis of diverse C_{3v}-symmetrical tetraammoniumtriptycene derivatives to overcome solubility issues. The synthesized triptycene derivatives are potential precursors for the synthesis of giant macrocycles or cage compounds.

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Keywords: *macrocycles;*

P-0898

THE SYNTHESIS AND PROPERTIES OF NEW CARBAZOLE-CONTAINING COMPOUNDS

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A lot of interest in carbazole-containing compounds was caused by the discovery of photoconductivity in poly(N-vinylcarbazole) by H. Hoegl. In 1957, he has established that PVK sensitized with suitable electron acceptors showed high enough levels of photoconductivity to be useful in practical applications like electrophotography. As a result of the following activities, IBM introduced its Copier I series in 1970, in which an organic photoconductor, the charge transfer complex of PVK with 2,4,7-trinitro fluorenone was used for the first time.

The ongoing peak of interest in carbazole-containing compounds in connected mostly with the discovery of polymeric light emitting diodes and organic photorefractive materials. Apart from electrophotographic photoreceptors, light emitting diodes and photorefractive materials carbazole-containing compounds are studied as components of photovoltaic devices. In all these fields of application of their ability to transport positive charges (holes) are exploited.

In this work, the reaction of carbazole with triethylaluminum has been studied and in the next step product of this reaction has been exposed to cyclic anhydrides and other heterocyclic compounds (esters, carbonates) in order to examine the direction of ring opening and to initiate polymerization.

The reaction of carbazole with triethylaluminum formed diethyl(N-carbazolyl)aluminum, which undergoes aggregation and occurs in dimeric form. Monomer and dimer in solution are in equilibrium, and their proportion vary depending on temperature and concentration. The reaction of diethyl(N-carbazolyl)aluminum with cyclic anhydrides, esters or carbonates followed by ring opening and incorporation of compound between aluminum and nitrogen. Additionally, in an easily polymerization cyclic esters such as ε-caprolactone and lactide, followed by initiating polymerization. Acid hydrolysis of the reaction mixture can be obtained from the reaction of cyclic anhydrides - acids, and the reaction of cyclic esters or carbonates - alcohols, which in its structure contains carbazole.

Keywords: *carbazole; triethylaluminum; anhydrides; cyclic esters;*

P-0899

SYNTHESIS OF AROMATICS VIA THE C-C BOND ACTIVATION

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Whereas different methods for creation of new C–C bonds are basic elements in organic synthesis, procedures which use cleavage of such bonds are not very common. Synthetic approach based on the C–C bond cleavage can be conveniently applied on strained carbocycles such as cyclopropanes and cyclobutanes, because it is driven by release of the ring strain..

Biphenylene is a typical compound bearing the strained cyclobutane ring. Therefore it easily undergoes oxidative addition with many transition metal complexes (Ir, Rh, Ni, Co, Fe, Pd, Pt) forming metallacyclopentanes[1]. We focused on the catalytic cycloaddition of biphenylene with alkynes and nitriles in the presence of iridium and rhodium complexes. Through this method a large number of substituted phenanthrenes (including ferrocenylphenanthrenes) and phenanthridines (new methodology) were synthesized[2]. The reaction of biphenylene proceeded even with sterically hindered diferrocenylacetylene giving rise to the corresponding 9,10-diferrocenylphenanthrene in a good isolated yield (42%). Our alkyne insertion procedure was also applied on the more complexed system such angular [3]phenylene exclusive and unexpected selectivity of the course of the reaction was observed (addition from the sterically disfavoured side).

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Keywords: *iridium; Rhodium; C-C activation;*

P-0900

SYNTHESIS OF PALLADIUM(II) COMPLEX WITH 2-(PHENYLSELENOMETHYL)TETRAHYDROPYRAN

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The use of organoselenium compounds as ligands in transition metal coordination chemistry has deserved special attention, in part as a result of the recognition that they may confer significantly different properties on the resultant complexes[1]. In addition, many organoselenium compounds play important roles in biochemical processes, ranging from antioxidant, to anticancer and antiviral activities[2].

In order to study biological activity, Pd(II) complex with 2-(phenylselenomethyl) tetrahydropyran as ligand was synthesized. It is noteworthy to mention that this kind of ligand compounds can be easily obtained in high yields via phenylselenoetherification of corresponding unsaturated alcohols in the presence of additives, such as pyridine[3]. For synthetic procedure, $PdCl_2$ and ligand were used in ratio 1:1. Single crystals were obtained after slow evaporation of complex compound from ethanol/methanol solvent system. The crystal and molecular structure of the complex $[Pd(L)_2)]Cl_2$ has been determined by X-ray diffraction. It turned out that two ligands are coordinated to the Pd via Se atom in *trans*-fashion and the other two *trans* position are occupied by Cl atoms.

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Keywords: *selenium; heterocycles; palladium;*

P-0901

SYNTHETIC STUDIES TOWARD SELECTIVE AND STABLE INHIBITORS OF DNA POLYMERASE ALPHA: CARBOCYCLIC ANALOGS OF DEHYDROALTENUSIN

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DNA polymerases play a key role in replication and maintaining of genome stability and some of them can help cancer cells tolerate DNA damage. Their selective inhibition is therefore considered viable strategy for therapeutic intervention in oncology.[1] Accordingly, depletion of DNA polymerase alpha (pol alpha) combined with inhibition of CHK1 kinase afforded synthetic lethal phenotype in cancer cells.[2]

Dehydroaltenusin is virtually the only known sub-micromolar selective inhibitor of pol alpha[3] that exhibited *in vivo* biological activity (include mice HeLa xenograft model).[4] However, the mechanism of action and potential usefulness of dehydroaltenusin are rather questionable as the compound is unstable and in polar solvents it exists as equilibrium mixture of two species: tricyclic lactone and its spirocyclic isomer.[5]

We have prepared racemic carbocyclic analogs of both forms of dehydroaltenusin. The target structures as well as some of the key intermediates contain novel, potentially useful pharmacophores. As the compounds are chemically stable, they could serve as appropriately robust chemical biology probes and good starting points for further medicinal chemistry optimization.

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Keywords: *Medicinal chemistry; Inhibitors; Spiro compounds;*

P-0902

SUPERBASE PROMOTED STEREOSELECTIVE AZETIDINE SYNTHESIS

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In the framework of an ongoing research project optically active 2-3-disubstituted oxetanes were prepared in our laboratory via superbase induced enantioselective rearrangements of chiral benzyloxymethyl oxiranes[1, 2]. From these oxetanes pyrrolidine derivative can be formed from in three steps[3].

Starting from that findings, our new aim was the further investigation of the stereoselective intramolecular rearrangement reaction with the intetntion to get azetidine derivatives. First we prepared oxirane derivatives which are substituted with benzylaminomethyl group instead of benzyloxymethyl function.

These compounds were treated with LIDAKOR superbase. The reaction provided the desired new azetidine derivatives containing the ring substituents in *trans* position, exclusively. The 1-methyl-2-phenyl-3-(1-(trimethylsilyloxy)-2-(trityloxy)ethyl)azetidine was prepared by TMSCl from the 1-(1-methyl-2-phenylazetidin-3-yl)-2-(trityloxy)ethanol. Now we try to prepare pyrrolidine derivatives from this compound.

The derivatives of the synthesized compounds can be valuable intermediates of drugs in pharmaceutical research[4], and can be used as chiral ligands in enantioselective catalytic reactions.

This work is connected to the scientific program of the “Development of quality-oriented and harmonized R+D+I strategy and functional model at BME” project. This project is supported by the New Hungary Development Plan (Project ID: TÁMOP-4.2.1/B-09/1/KMR-2010-0002) and was carried out in the framework of a bilateral scientific cooperation between the Hungarian Academy of Sciences and CNR Italy.

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Keywords: *superbase; rearrangement; enantioselective synthesis; heterocycles; azetidines;*

P-0903

DESIGN AND APPLICATION OF NEW IMIDAZOLYLSULFONATE BASED BENZYNE PRECURSOR: AN EFFICIENT TRIFLATE ALTERNATIVE

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Arynes are reactive intermediates due to their strained structure caused by the presence of distorted triple bond in the six membered carbacycle. This exotic compound class can be transformed efficiently in nucleophilic or electrophilic reactions, in pericyclic reactions and in transition metal catalyzed reactions. To exploit the advantages of imidazolylsulfonates over triflates we aimed to design new benzyne precursor family for organic syntheses.

Several o-(trimethylsilyl)aryl imidazolylsulfonates were synthesized in a simple process and successfully applied in cycloadditions involving benzyne intermediates. The precursor offers an efficient alternative for generating benzynes compared to widely used ortho TMS triflates under similar reaction conditions. With the utilization of this new precursor, the formation of potentially genotoxic trifluoromethanesulfonate side product is eliminated. Applicability of the new benzyne precursor was demonstrated in different type of cycloaddition reactions to prepare heterocyclic molecules.

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Keywords: *Arynes; Cycloaddition;*

P-0904

SYNTHESIS OF 7-ARYL- AND 7-(AMINOARYL)GUANINES

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Position *N*7 at guanine is a prominent site of attack by electrophiles in the DNA. Various electrophilic compounds can bind to this position *in vivo* causing DNA damage. Therefore, 7-alkyl- and 7-arylguanines are needed as analytical standards for studies on the DNA damage by mutagens and carcinogens. N^2-(Dimethylaminomethylene)guanine has been described previously as a suitable guanine precursor affording predominantly 7-arylderivatives by reaction with arylboronic acids in the presence of copper(II) ions (Keder et al., 2009).

We used this procedure for synthesis of 7-(3,4--Dihydroxyphenyl)guanine, which was prepared by treating N^2-(dimethylaminomethylene)guanine with 3,4-dimethoxyphenylboronic acid and subsequent deprotection. The same substrate was used for synthesis of 7-(2-aminophenyl)guanine and 7-(4-aminophenyl)guanine. In this case, N^2-(dimethylaminomethylene)guanine was arylated by corresponding fluoronitrobenzene. Predominating *N*7-isomer was separated from its mixture with *N*9-isomer, amino group deprotected by hydrolysis and, finally, the nitro group was reduced with hydrogen on palladium to afford 7-(aminophenyl)guanine in moderate yield.

Arylation of N^2-(dimethylaminomethylene)guanine by fluoronitroarenes seems to be a promising synthetic route to 7-(aminoaryl)guenines.

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Keywords: *arylation; arylguanines; DNA adducts;*

P-0905

TOWARDS THE TOTAL SYNTHESIS OF BETICOLIN 0

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Background: Beticolins are mycotoxins produced by the phytopathogen *Cercospora beticola* and are responsible for the leaf spot disease (cercosporiosis) on sugar beet. Biological studies on Beticolins revealed a broad cytotoxic profile by the interaction with different cellular targets and the ability to dimerize to non-specific ion channels. All Beticolins share the same unique polycyclic carbon skeleton consisting of a mono-chlorinated xanthone- and a tetrahydro-anthraquinone subunit. Both subunits are forming a hydrophobic bicyclo[3.2.2]nonane ring system what is a distinguished structural feature of this natural product class.

Results: In spite of their unique structure and their broad biological profile, any synthetic studies towards the synthesis of beticolins were not published yet. Preliminary experiments revealed that the anthraquinone moiety (A,B,C-ring-system) and the quarternary center of Beticolin can be constructed by a quinoid Diels–Alder reaction. This reaction can be enabled either by irradiation or by the use of organocatalysts. Using the latter, the asymmetric synthesis of the tricyclic unit is currently examined by the application of enantiopure catalysts. The formation of the unique bicyclo[3.2.2]nonane ring-system *via* a metal-catalyzed cross-coupling reaction is also under current investigation. The completion of the carbon skeleton of Beticolin 0 should be accomplished by the synthesis of the remaining tetrahydroxanthenone moiety with a domino-Oxa–Michael-aldol-reaction.

Conclusion: Synthetic efforts provided access to the A,B,C-ring system of Beticolin. These results are also of importance for the synthesis of the biosynthetically related xanthoquinodins and acremoxanthones.

Keywords: *Natural Products; Cytotoxicity;*

P-0906

SYNTHESIS OF 5-ALKYLIDENE-1,2,5,6-TETRAHYDROPYRIDIN-2-ONES RELATED TO GELASTATINS

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Compounds with 5,6-dihydro-2H-pyran-2-one skeleton occur in nature and possess wide range of biological activities from antibacterial effects to cytotoxicity[1]. Given these interesting properties, our research in recent years was focused on gelastatins A and B [2]. These molecules (isolated from *Westerdykella multispora*) have shown the ability to inhibit gelatinase A, a metalloproteinase participating on degenerative inflammatory processes and penetration of tumour cells into healthy tissues[3].

Over the past few years, our group has synthesized 3,5-disubstituted 5,6-dihydro-2*H*-pyran-2-ones with an alkylidene substituent at C5 [4], which possess interesting cytostatic activity. Regrettably, these compounds suffer from low stability. The purpose of this work has been to develop the synthesis of analogous lactams, which should be more stable and also more water-soluble than their lactone counterparts and investigate their chemical properties as potential Michael acceptors.

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Keywords: *Lactams; Nucleophilic addition; Palladium;*

P-0907

SYNTHESIS OF FERROCENE-BASED MOLECULAR WIRES

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Molecular wires of the oligo(phenylene ethynylene) (OPE) type have rigid structures with fixed molecular lengths. To introduce limited conformational flexibility we are interested in replacing some 1,4-phenylene units by 1,1'-ferrocenylidene groups. Different molecular wires with two or three ferrocene units with *tert*-butylsulfanyl groups as anchoring groups were obtained via Sonogashira coupling reaction or Negishi coupling reaction.[1, 2]

In search for different anchoring groups we noted that Wandlowski reported about molecular wires with nitrile groups.[3] First examples for nitrile-terminated molecular wires based on ferrocene have recently been prepared.

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Keywords: *Ferrocene; OPE; Molecular Wire;*

P-0908

APPLICATION OF CHIRAL RUTHENIUM CATALYSTS IN ENANTIOSELECTVIE OLEFINMETATHESIS

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The development of chiral Ru-based olefin metathesis catalysts to obtain high enantioselectivities has been shown to be a challenge in the field of asymmetric olefin metathesis. Recently we reported the development of highly active and chiral Ru-based metathesis catalysts with high stability which show excellent results in asymmetric ring-opening cross metathesis (AROCM) as well as in enantioselective ring-rearrangement metathesis (*e*RRM).

Various cross partners such as allylsilanes, allyl alcohol, allyl chloride and allyl *tert*-butyl carbonate can be used in the AROCM of norbornene derivatives providing products with high *E*-selectivity and excellent enantioselectivities up to 93%*ee.* The AROCM products with allyl silanes can further be transformed in a *Sakurai* reaction into highly enantiomerically enriched bicyclo[3.2.0]heptanones with 4 stereogenic centers which contain a new built 4-membered ring.

Ring-rearrangement metathesis is a well-known and powerful method to construct complex carbo- and heterocycles in a domino process that has been used in several natural product syntheses. Nevertheless efficient enantioselective RRM still remain challenging.

Here the first examples of asymmetric Ene-Yne-RRM based on chiral Ru-metathesis catalysts were performed providing excellent enantioselectivities up to 94%*ee* giving tetrahydropyridines selectively.

Keywords: *metathesis; domino reactions; ruthenium; enantioselectivity; regioselectivity;*

P-0909

SYNTHESIS AND PROPERTIES OF UNIQUE ARENDIAZONIUM SALTS WITH LIPOPHILIC NATURE

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Arenediazonium salts are widely used in classical organic synthesis and in the preparation of modern organic nanocomposites and the grafting of organic molecules onto metallic or non-metallic surfaces. A new type of diazonium salts – arendiazonium dodecylsulfonates (ADDS) was firstly obtained by diazotization of aromatic amines in the presence of dodecylsulfonic acid at room temperature with 50-80 % yields. ADDS have unique solubility in both polar and nonpolar (benzene, hexane, tetrachloromethane) solvents and stability in dry state and in solutions. The lipophilic nature of ADDS can open new possibilities for usage of diazonium compounds in organic synthesis.

ADDS have typical diazonium nature, giving the products of azo-coupling and aryliodides by the reaction with KI in quantitative yields. Also their high reactivity in C-C-coupling reaction was demonstrated. Thus, a new method of olefins arylation in water in the presence of palladium catalysts under microwave irradiation with excellent yields of target products was proposed.

In conclusion, a new arenediazonium dodecylsulfonates as a previously-unknown class of diazonium salts was prepared in a pure, dry state. Due to their unique amphiphilic nature it is firstly possible to carry out diazonium reactions in nonpolar media in the absence of phase-transfer catalysts. Because of their stability, they can be stored safety for a long time. It is especially interesting that these salts reveal good solubility in nonpolar solvents and high reactivity in a typical reaction of diazonium salts and C-C-coupling reactions.

Keywords: *Diazo compounds; Amphiphiles; C-C coupling;*

P-0910

SPECTATOR FERROCENYL SUBSTITUENT: PKAS OF PLANAR CHIRAL PYRIDINE ORGANOCATALYSTS

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Leading the advances in new asymmetric methodology, Fu and co-workers developed planar chiral organocatalysts derived from 4-(dimethylamino)pyridine. The coupling of a ferrocenyl group to a pyridine ring introduced asymmetry into the system and this has proved to be highly efficient, high yielding, and most importantly, highly enantioselective for a range of reactions.[1]

As part of a mechanistic investigation of the role of these organocatalysts in several transformations routes to additional derivatives of the catalyst with varying substituents at the 4-position of the pyridine ring were developed. These include the 4-methoxy, 4-chloro and the unsubstituted parent catalyst.

The pK_a values for the conjugate acids of the pyridine-ferrocenyl catalyst and novel analogues in dry dimethyl sulfoxide and acetonitrile have been measured employing a UV-Vis spectrophotometric bracketing buffer method.[2] Due to rapid decomplexation of the conjugate acid forms of novel analogues the application of stopped-flow spectrophotometry was required to determine the pK_as rather than conventional UV-Vis spectrophotometry.

pK_a values from 12.8 to 19.9 were recorded in acetonitrile and 3.3 to 10.3 in dimethyl sulfoxide. A comparison of the measured pK_as for the pyridine-ferrocenyl catalysts with analogous achiral pyridinium ions revealed no significant effect, consistent with a spectator role for the ferrocenyl substituent on pK_a. The role of ion pairing and addition of up to 5 vol% H_2O on the pK_a was also assessed.

These pK_a values may be used in a Bronsted analysis of arylalkyl ketene-nucleophilic addition reactions catalysted by these planar chiral pyridine organocatalysts for the purpose of mechanistic evaluation.

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Keywords: *Bronsted acid-base; Organocatalysis; Asymmetric catalysis; Reaction mechanisms; UV-Vis spectroscopy;*

P-0911

FUNCTIONALIZED VESICLES IN MOLECULAR RECOGNITION - VISUALIZATION AND BINDING AFFINITIES

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Non-covalent interactions of receptors and ligands at liposomal surfaces are very similar to recognition processes at biological membranes. Molecular recognition on such membranes is often governed by dynamic multivalent interactions. Based on previously reported vesicular chemosensors for the recognition of small biomolecules,[1] we currently focus on more complex liposomal systems with different artificial binding sites for the dynamic recognition of multivalent target molecules.

The visualization and determination of binding affinities of such multi-receptor surfaces requires a lot of different methods and techniques.

For the visualization of liposomes we use dynamic light scattering (DLS), fluorescence microscopy, atomic force microscopy (AFM) and cryogenic temperature transmission electron spectroscopy (Cryo-TEM).

For the determination of binding affinities between doped liposomes and suitable analytes fluorescence based binding assays are already established very well. Besides we developed a surface plasmon resonance (SPR) based assay for the determination of binding constants for the interaction between functionalized surfaces and proteins, peptides and other analytes.

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Keywords: *liposomes; molecular recognition; supramolecular chemistry; surface chemistry; metal complexes;*

P-0912

THE BIOSYNTHESIS OF MURAYMYCINS: SYNTHESIS OF POTENTIAL INTERMEDIATES FOR STUDIES ON THE ASSEMBLY OF COMPLEX NATURAL PRODUCTS

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The *Streptomyces*-produced muraymycins (*e.g.* muraymycin A1), a subclass of nucleoside antibiotics, are potent inhibitors of bacterial cell wall biosynthesis.[1] Due to their structural complexity, the synthesis of new muraymycin analogues is challenging. Detailed investigations on the biosynthesis of this important family of natural products could provide access to new muraymycin derivatives through fermentation-based production of unusual building blocks, such as the non-proteinogenic amino acid epicapreomycidine, a cyclic arginine derivative. The biosynthesis of the 3-epimer of epicapreomycidine, capreomycidine, has been elucidated and utilises (3*S*)-3-hydroxy-l-arginine as an intermediate.[2] Thus it is proposed that 3-hydroxy-l-arginine also serves as an intermediate in the biosynthesis of epicapreomycidine and therefore also in the formation of muraymycins in *Streptomyces*. Both potential intermediates (3*R*)-3-hydroxy-l-arginine and (3*S*)-3-hydroxy-l-arginine have been synthesised using a novel route suitable for multiple isotope labelling.[3]

Recently, the gene cluster for muraymycin biosynthesis has been identified, sequenced and analysed by Cheng *et al*. Homology studies led to a proposed pathway for muraymycin biosynthesis.[4] Using both diastereomers of isotope-labelled 3-hydroxy-l-arginineand other potential intermediates this outline proposal can be tested experimentally.

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Keywords: *Antibiotics; Amino acids; Biosynthesis; Isotopic labeling; Nucleosides;*

P-0913

SYNTHESIS OF POLYOXOMETALATE-POLYMER HYBRIDS VIA RAFT POLYMERIZATION

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Organic hybrids of polyoxometalates (POMs) - molecularly defined, anionic nanosized metal oxygen clusters of highly oxidized early transition metal cations (W, Mo, V) – have attracted considerable interest over the past few years due to their specific properties.

This work aims at the synthesis of POM-polymer conjugates which can be obtained by two strategies. In the first one, the « grafting to » approach, the polymer is firstly synthesized and then covalently linked to the POM (post-functionalization).[1, 2] The second approach, the « grafting from » one, is based on polymer growth from a POM-based initiator.[3] To date, there are three different POM-polymer hybrids reported, obtained by controlled radical polymerization.[1, 2, 3]

Here, we focus on the synthesis of thermoresponsive polyoxometalate-polymer hybrids, via Reversible Addition-Fragmentation Chain Transfer (RAFT) polymerization using a « grafting from » approach (Scheme 1). We worked on Dawson-type polyoxometalates, which were functionalized with a trithiocarbonate reactive group. This precursor was used to synthesize conjugates containing different polymer lengths. The thermoresponsive properties of the conjugates in water were studied.

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Keywords: *Polyoxometalates; polymerization; aggregation; polymers; Organic-inorganic hybrid composites;*

P-0914

TOTAL SYNTHESIS OF FUSARISETIN A

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The first total synthesis of (-)-fusarisetin A, the enantiomer of naturally occurring acinar morphogenesis inhibitor (+)-fusarisetin A, was accomplished, leading to the reassignment of the absolute configuration of the natural product. The synthesis featured a Lewis acid-promoted intramolecular Diels-Alder reaction, a Pd-catalyzed O?C allylic rearrangement, a chemoselective Wacker oxidation, and a Dieckmann condensation/hemiketalization cascade.

Keywords: *total synthesis; cell migration/invasion inhibitor; intramolecular Diels-Alder; Wacker oxidation; Pd-catalyzed O?C allylic rearrangement;*

P-0915

SOLID STATE PHOTOPOLYMERIZATION OF A SHAPE-PERSISTENT MACROCYCLE WITH TWO 1,8-DIAZAANTHRACENE UNITS TO A RIGID-ROD POLYMER IN THE SINGLE CRYSTAL

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A shape-persistent macrocyclic monomer with two opposing 1,8 diazaantharcene photoreactive units is polymerized in the single crystal by photochemically induced [4 + 4]-cycloaddition reaction between neighboring monomers in which the diazaanthracene units are face-to-face stacked at the critical Schmidt-distance. The severe structural changes associated with this are compensated by the monomer design whereby the linkers between the two opposing 1,8-diazaanthracenes are connected to the 1 and 8 positions of the latter. It is those sites whose spatial positioning suffers the least change during dimerization and thus helps keeping the monomer's overall shape basically unchanged during polymerization. The resulting new rigid-rod polymer is soluble in its protonated form and can be depolymerized after counter ion exchange with a surfactant in an organic solvent upon relatively mild thermal treatment (120 °C) back into monomer.

Keywords: *Solid state photopolymerization; rigid-rod polymer; diazaanthracene; depolymerization;*

P-0916

NOVEL BODIPY LABELLED CYCLODEXTRIN PROBE

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Fluorescence labels have nowadays a wide field of application, ranging from analytical chemistry, molecular biology and biotechnology to medical applications. Due to the high sensitivity, fluorescence phenomena are the methods of choice for studying processes such as release kinetics of agents in cells. Numerous different classes of fluorescent dyes have been established over the years. Among them 4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (BODIPY) based dyes are widely used because of their chemical and physical stability, high molar extinction coefficients and fluorescence quantum yields, sharp absorption and emission bands.[1] One disadvantage is their poor solubility in water.

Cyclodextrines are cyclic oligosaccharides, which possess a hydrophilic exterior and a hydrophobic cavity: They form easily inclusion complexes with appropriate hydrophobic guest molecules in aqueous media.[2]

We report here on the synthesis, characterization and possible applications of a novel BODIPY labelled cyclodextrin derivative, with high solubility in water and very interesting fluorescence properties. The labelling reaction causes a considerable blue shift of both the absorption and emission maxima of the dye, which offers an easy method for observing the successfulness of the reaction. This new fluorescence probe can be used to study the properties and behaviour of inclusion complexes with optical inactive guest molecules in various environments.

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Keywords: *Cyclodextrin; Bodipy; Fluorescence;*

P-0917

NOVEL HIGHLY LUMINESCENT POLYMERS

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Luminescent polymers are of great scientific and industrial importance for example for the production and improvement of organic light emitting diodes (OLED).[1]

We describe the synthesis and characterization of several new pi-conjugated, fluorescent polymers. The macromolecules contain electron rich arylether and/or electron poor aromatic N-hetereocycles such as pyrazine. Good solubility in common organic solvents is achieved by using long alkyl or oligoethylenglykol groups. The polymers are built up by a combination of Horner-Wadsworth-Emmons-, Sonogashira reaction and/or Glaser-coupling of several different buildingblocks. The macromolecules show interesting absorption and emission wavelengths and an overall good solubilities.

Due to their centro-symmetrical structure and the presence of donor and acceptor groups these polymers are hopefully good candidates for two-photon exited fluorescence.

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Keywords: *Oled; Polymers; Fluorescence;*

P-0918

TRANSFORMATION OF INORGANIC HALOGENS TO CHLORINATED HYDROCARBONS BY ENZYMES

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Biogeochemical cycle of chlorine, particularly formation of organically bound chlorine (Cl_{org}), is still known only in outlines. In continental ecosystems chloride acts as stress factor, and also as source of chlorine; it originates from precipitation, which comes from marine cloud masses. Cl_{org} are formed naturally by biotical and abiotical way. The biological factors are microorganisms, soil enzymes, plants and even animals. Halogenation processes undergo in marine environment as well, the main difference is the presence of bromine besides chlorine, therefore the reaction and formation of brominated compounds. One group of Cl_{org} represents volatile chlorinated hydrocarbons (VOCl). Several VOCl can react with atmospheric ozone, consequently causing its depletion. The best known sources of VOCl are soil, the microorganisms living in it, and their exoenzymes released into it.

The heme peroxidases in the group EC 1.11.1 can perform halogenation of organic compounds. Hydrogen peroxide or organic peroxides are the substrates of this reaction in which hypochlorous acid is generated. The halogen in reactive form then carries chlorine onto the organic compound.

To study enzymatic mediation of chlorination processes, we chose commercially available enzymes (chloroperoxidase from *Caldariomyces fumago* and horseradish peroxidase). To concentrate the formed analytes, we used solid-phase microextraction (SPME) method or cryofocusing method, followed by GC-ECD or GC-MS analysis.

The formation of VOCl was confirmed in experiments, where enzyme, citric acid buffer, halogen ions (KBr, NaCl) and substrates (acetic acid, aceton) were present. Contrary to the literature, both enzymes formed chlorinated and brominated volatile compounds. The main volatile organic chlorinated compounds were chloroform, bromoform, trichloroethylene, tetrachloroethylene, halogenated methane derivatives and aliphatic compounds. The formation was dependent on the length of the enzyme reaction.

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Keywords: *chlorine; gas chromatography; halogenation; enzyme catalysis; bromine;*

P-0919

NOVEL 1,2,3-TRIAZOLE FUNCTIONALIZED PENTACENE COMPOUNDS: SYNTHESIS AND CHARACTERIZATION

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Organo-electronic materials have gained raising scientific and commercial interest in recent years due to various advantages compared to inorganic semi-conductors.[1] Outstanding electronic properties of acenes, relying on the topology of the π-systems, led to intense research efforts on this compound class.[2] In particular pentacene proved to be a benchmark p-type organic semiconductor for applications such as organic field effect transistors (OFETs) and organic photovoltaics (OPVs).[1] In the recent years Anthony *et al.* revealed that also the functionalization of acene derivatives results in highly efficient semi-conductive materials by improved molecular stacking.[1, 2]

Typical drawbacks of acenes are the relatively low solubility (which is of great technological interest) and stability (e.g. oxidation and dimerization) of these compounds.[2, 3] Hence, it was shown that the attachment of electron withdrawing groups to the 6- and 13-position of pentacene significantly improves the stability towards oxidative processes.[3]

In this contribution we focus on the symmetric bis-functionalization of the pentacene moiety with 1,2,3-triazole moieties in the 6- and 13-positions. As previously described in the course of investigations on nonlinear optical (NLO) materials the 1,2,3-triazole moiety exhibits interesting electron accepting properties.[4] Thus, the effects on stability, solubility and molecular arrangement (examined also in OFET devices) are content of this investigation.

The synthetic concepts are based on the application of organo-lithium mediated procedures, $SnCl_2$ assisted aromatization and Cu(I) catalyzed azide-alkyne cycloaddition (CuAAC), one of the most popular reactions in the click chemistry concept,[5] yielding the target compound starting form readily available 6,13-pentacenequinone.

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Keywords: *pentacene; triazole; ofet; click;*

P-0920

A MODERN APPROACH TOWARDS THE SYNTHESIS OF [18]ANNULENE

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As of this writing, only two successful syntheses towards [18]annulene were reported. The first was reported in 1962 by Sondheimer and Wolovsky, starting from 1,5-hexadiyne in three steps and 0.6% overall yield.

The second synthesis was reported in 1970 by Figeys and Gelbcke in five steps, starting from propargyl alcohol to yield 0.42% [18]annulene.

Although determined by X-ray structure, the structure of [18]annulene remains controversially discussed by many scientists. Therefore, we developed a new and efficient route towards [18]annulene. This three-step synthesis is not only more practical and safer in today's laboratories, but also increases the yield by more than 700% compared to earlier published routes. Starting from *cis*-1,2-dichloroethene, we utilized the Sonogashira cross-coupling reaction to produce TMS-protected hexaenediyne, which is then deprotected and trimerized in one pot to hexadehydro[18]annulene. The reduction via Lindlar-catalyst gives the target molecule in 4.4% overall yield. Although we cannot show definite prove, we provide experimental and computational evidences that a lower symmetry, such as D_{3h} or C_2, appears more realistic for [18]annulene rather than D_{6h}-symmetry.

Keywords: *Annulenes; Aromaticity; Cross-coupling;*

P-0921

BITHIOPHENESILANE-BASED DENDRITIC MACROMOLECULES: SYNTHESIS AND PROPERTIES

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Dendrimers are unique organic materials, which combine highly branched regular arrangement of functional organic moieties within one macromolecule having typical dimensions of 1 to 10 nm. Oligothiophenesilane dendrimers are known for their efficient molecular antenna effect[1], as well as intensive photoluminescence in the violet-blue region, the quantum yields of which are significantly higher than those measured for their constituent luminophores themselves[2]. The main drawback of the high-molecular weight dendrimers is their multistage synthesis, which limits their practical applications. This problem may be solved by the synthesis of dendronized polymers. These unique materials combine the properties of both dendrimers and polymers. They are currently are under intense investigation with respect to various applications, including the synthesis of hierarchically structured materials, catalysis, applications in the biosciences, such as ion channel mimics and DNA compactization, as well as optoelectronic applications[3]. We report here the synthesis and investigation of several generations of bithiophenesilane-based dendrimers and dendronized polymers[4] as well as preliminary application of the most perspective molecules in organic light-emitting diodes.

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Keywords: *dendronized polymers; dendrimer; luminescence;*

P-0922

NEW CARBOCYCLIC NUCLEOSIDE ANALOGS

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Nucleoside analogs encompass a variety of biologically active compounds, namely those with antiviral and anticancer properties. Significant efforts have been invested in order to prepare nucleoside analogs possessing new structural motifs[1]. Carbocyclic nucleoside analogs have been particularly attractive as the tetrahydrofuran moiety can often be replaced with more metabolically stable carbocycles without significant loss of activity[2]. Nevertheless, cyclopentane nucleoside analogs (especially those with the base attached via C-C linkage) are quite rare and most published syntheses produced only single target compounds[3].

Of biologically active carbocyclic nucleoside analogs, pseudoisocytidine proved active against cytarabine-resistant leukemias and showed resistance toward deamination mediated by cytidine deaminase[4], but its hepatotoxicity (of unknown origin) in humans halted the clinical progression[5]. We have synthesized the direct carbocyclic analog of pseudoicytidine and additional compounds with differently substituted pyrimidine base parts.

In addition, we have developed flexible synthesis of cyclopentane nucleoside analogs possessing tertiary OH at the 1'-position. Unlike the tetrahydrofuran-containing analogs, the compounds are chemically robust. Our methodology enables selective manipulation of individual positions around the cyclopentane ring.

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Keywords: *nucleosides; synthetic methods; drug design;*

P-0923

AN OXIDATIVE COUPLING ROUTE TO MACROCYCLIC THIOPHENES AND ITS APPLICATION IN THE SYNTHESIS OF A DONOR/ACCEPTOR HYBRID MOLECULE

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Thiophene-containing macrocycles are known for their unique optoelectronic properties and their ability to form supramolecular structures.[1] Yet, their synthesis is difficult, and ring closure is rarely performed at the thiophene sites themselves.

Here we present a cyclooligomerization approach towards macrocyclic thiophenes *via* direct oxidative coupling of unfunctionalized thiophenes.[2]

The synthetical concept was applied to prepare a thiophene macrocycle with covalently attached perylenbisimide units. In this donor/acceptor hybrid structure a highly efficient electron transfer can be induced by optical excitation of either one of the subunits.[3]The molecule forms supramolecular 2D assemblies at the solid/liquid interface that were investigated by scanning tunnelling microscopy. Chain-like structures were observed, consistent with strong stacking interaction of adjacent perylenebisimide units.

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Keywords: *Cyclooligomerization; Donor-acceptor systems; Macrocycles; Electron Transfer; Self-assembly;*

P-0924

SENSING FLUORIDE WITH TREN RECEPTORS THROUGH ELECTROSTATIC INTERACTIONS AND HYDROGEN BONDING

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Developing a receptor for fluoride anion is challenging task because of its high hydration energy, small ionic radius and hardness as Lewis base making fluoride sensing difficult particularly in aqueous environment.[1] Due to these still unresolved challenges scientific community is pursuing to develop more specific and stronger receptors for fluoride.

In this study we have developed simple TREN [tris(2-aminoethyl)amine] based aromatic receptors having three amide groups and three nitro-functionalized aromatic rings. Receptors are synthesized with microwave-assisted method using previously reported tripodal molecules that has been shown to bear the ability to bind fluoride.[2] Binding is achieved via pre-organization of the receptor, amide group mediated hydrogen bonds and electrostatic interactions. The binding process has been studied with variety of methods both in solvent and solid states. The interaction between the receptor and the fluoride anion is clearly seen for example by NMR measurements.

Even though these receptor are demonstrated to bind fluoride in polar aprotic DMSO which is suitable media for anion recognition, similar kinds of receptors could possibly be used for fluoride recognition also in aqueous environment. There is ongoing study in our laboratory to develop this receptor-type further and to reach the ultimate goal in fluoride sensing, recognize it in water.

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Keywords: *Anion recognition; Fluoride;*

P-0925

ANIONIC POLYMERIZATION OF EPSILON-CAPROLACTONE INITIATED BY ETHYL MAGNESIUM BROMIDE

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Poly(ε-caprolactone) is well-known biocompatible and biodegradable polymer which can be prepared by either of ring-opening polymerizations of ε-caprolactone using a variety of anionic, cationic and coordination initiators. The best known initiators of the ε-caprolactone polymerization are aluminum tri(isopropoxide) and tin(II) 2-ethylhexanoate with co-initiator (mostly an alcohol). Magnesium compounds are used as initiators in the ε-caprolactone polymerization like magnesium lactate, magnesium octoate, magnesium alkoxides etc.

We have focused on the study of solution polymerization of ε-caprolactone initiated by ethyl magnesium bromide which is rather neglected in literature. The ε-caprolactone polymerization was carried out in dry toluene at 0 and 25 °C and at two monomer/initiator ratios (250 and 500) in order to describe polymerization course. For comparison, we also proceeded a reference solution polymerization of ε-caprolactone initiated by tin(II) 2-ethylhexanoate. Polymerizations initiated by ethyl magnesium bromide proceeded by a living fashion and, in the initial phase of the process molar mass was controlled by the monomer/initiator ratio. The polymer in the initial phase of the process has a narrow molar mass distribution. This is explained by the formation of the complex of magnesium initiator with carbonyl groups of ε-caprolactone and polyester formed which suppresses both intra- and intermolecular side reactions. The isolation and characterization of the magnesium/ε-caprolactone complex supports suggested mechanism of polymerization.

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Keywords: *polymerization; kinetics; magnesium;*

P-0926

SYNTHESIS OF THE ERYTHRINA ALKALOID ERYBIDINE BY A PHOTOCHEMICAL CYCLIZATION AND ITS STEREOCHEMICAL ANALYSIS

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Biaryl natural compounds are a widespread substance class with numerous pharmacological applications. Furthermore, they often show axial chirality. These are reasons why these compounds become increasingly important.[1]

Erythrina alkaloids are natural products found in the leaves of *Erythrina bidwillii*. Erybidine was shown to be 5,6,8,9-tetrahydro-2,11,12-trimethoxy-7-methyl-dibenz[*d,f*]azonin--3-ol.[2] This compound contains a biaryl axis, which offers the possibility of a non-obvious chirality. We investigated if the compound forms two atropoisomers due to inhibited rotation around the biaryl axis with only two *ortho*-substituents but additional ring strain.

We improved the synthesis of Erybidine formerly described in the literature.[3] The amide-coupling-step is changed and a photochemical intramolecular coupling with a 100 W high pressure mercury lamp yielded three different products. One of them gave rise to Erybidine.

The stereochemical behaviour of Erybidine at the biaryl axis was examined by racemization experiments and MD studies. Due to the two *ortho*-substituents and the cyclic structure of Erybidine free rotation around the biaryl axis is limited. Separation of the two atropoisomeres was effected by HPLC on a chiral column. Furthermore, the ring-size of the aza moiety plays an important role.

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Keywords: *natural products; alkaloids; axial chirality;*

P-0927

CU–VINYLPHOSPHONATE REVEALING SEMICONDUCTOR ELECTRICAL BEHAVIOR

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Starting from the X ray experimental data for Cu-vinylphosphonate (VP-Cu), a theoretical study was performed using cuanto-chemichal calculus using PM3 semiempirical method under Hyperchem 7. Strategy was based built models or extracted models from X ray data. From geometrical analysis, for VP-Cu it was observed that bonding lengths of C-C and Cu-O were all similar with the values found in literature[1]. Cu-O_w bonding lengths were slightly underestimated compared to X ray experimental data. From electronic properties of VP-nCu (n=2, 3, 4, 8), structures used as models to build VP-Cu compound, it was observed that the lowest LUMO-HOMO energetic difference is 2.933eV for VP-3Cu, revealing a potential semiconductor behavior.

For electrical conductivity measurements, a setup was built using a screw-nut type polyamide insulated fixture embedding two sliding conductive electrodes. The exact compound thickness between electrodes was confirmed by using an electronic microscope. For faster humidity and temperature settling of the compound, radial holes were practiced in electrodes area.

Measurements conditions were provided by a climatic chamber, and performed after 1h settling time for each combination between temperatures in 25–90°C range and relative humidity in 50–95% range. For conductivity measurement it was used cyclic voltammetry at low and fast speed. As voltage current dependence was found to have a linear dependence, independent on voltammetry speed, it was concluded that conduction takes place using electrons. By representing Arrhenius plot for conductivity it was possible to extract activation energy which was close to the cuanto-chemical estimated value, thus proving semiconductor behavior of the compound. Increasing conductivity with relative humidity indicates also potential applications for humidity sensors, and further experiments will determine electrical conductivity settling time versus humidity variations.

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Keywords: *Metal-organic frameworks; Semiconductors;*

P-0928

NEW EXTENDED POLYCONDENSED AROMATIC HYDROCARBON OF THE C60 CLASS

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Alkyl-substituted tribenzo[*fg*,*ij*,*rst*]pentaphenes (TBP) represent versatile polycondensed aromatic hydrocarbon building blocks exhibiting pronounced π-π stacking properties[1]. Best positions for placing the solubilizing alkyl side chains were determined by theoretical studies on the π-π stacking behavior. This investigations yielded exact geometries for minimum energies of stacked dimers.

A convenient synthesis for a 15,16-disubstituted derivative involves a Diels-Alder reaction between phencyclone and 8-hexadecyne followed by a classical Scholl oxidation under Kovacic conditions ($FeCl_3/CH_3NO_2$ in CH_2Cl_2 at r.t.) of the resulting diheptyl-diphenyl-terphenylene[2]. We were surprised to find that in this specific case intermolecular oxidative dimerization predominates over intramolecular aryl-aryl coupling, since we observe a triply connected completely oxidized dimer as a major product even before complete consumption of the starting material. The observation of a singly linked starting molecule as well as a singly linked but otherwise fully oxidized dimer (for which a 5,5'-link could be deduced from the ^{1}H-NMR spectrum), permitted us to propose a reaction sequence for this surprising transformation and to attribute a structure to the triply connected fully oxidized dimer, which otherwise failed to yield interpretable NMR spectra. Interestingly emission spectroscopy proved to be a sensitive tool since even slightest changes, e.g. concerning the location of side chains, were reflected in subtle changes of the emission spectra[3].

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Keywords: *Polycycles; C-C coupling; Pi interactions; Fused-ring systems; Dehydrogenation;*

P-0929

FLUORESCENCE ANISOTROPY OF BICYCLO[1.1.1]PENTANE/OLIGOPHENYL-BASED RODS INCLUDED IN TRIS(O-PHENYLENEDIOXY)CYCLOTRIPHOSPHAZINE

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Motion of rod-like molecules included into the channels of hexagonal (tris-o-phenylenedioxy)cyclotriphosphazine (TPP) have been examined in the past by NMR techniques. We now report an examination of this motion by fluorescence anisotropy measurements with time resolution in the fs range as a function of temperature, using suspensions of nanocrystals of TPP loaded with 0.02 - 2% of the guests. The included molecular rods, specially synthesized for the purpose, contained a fluorophore (such as quaterphenyl or pyridazine) held between two bulky groups (such as 1,3-disubstituted bicyclo[1.1.1]pentanes), which were found to fix the orientation of the long axis along the TPP channel direction. At high guest loadings, concentration depolarization interfered with the interpretation of the measurements, but in highly diluted samples this interference disappeared and the long molecular axis was found to exhibit no detectable motion, allowing us to focus on rotation around it.

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Keywords: *UV/Vis spectroscopy; Molecular rotors; Fluorescence anisotropy;*

P-0930

COMBINATORIAL SYNTHESIS AND EVALUATION OF A-IMINOCARBOXAMIDE-NICKEL (II) CATALYSTS FOR THE COPOLYMERIZATION OF ETHYLENE AND A POLAR MONOMER

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α-Iminocarboxamide structure is found in a lot of functional molecules. In particular, α-iminocarboxamide-nickel (II) complex has attracted much attention in recent years as a catalyst for the copolymerization of ethylene with functionalized monomers. The polymerization activities of this catalyst vary from small differences of functional groups in α-iminocarboxamide. However, combinatorial optimization of substituents has not been reported. We anticipated that the highly active catalyst could be discovered through constructing a combinatorial library consisting of a-iminocarboxamides with systematically modified substituents. Herein we wish to report the development of the efficient synthetic method of α-iminocarboxamides, and the evaluation of the ethylene polymerization and copolymerization activities of a-iminocarboxamide-nickel (II) catalysts prepared from synthesized a-iminocarboxamides.

We plan to synthesize α-iminocarboxamide by two routes. First route involves an amidation of the α-ketoacid chloride and a subsequent imination of the obtained ketone. Second route involves a three-component coupling of alkyl samarium (III) with isocyanide and isocyanate.

The amidation and imination conditions were efficiently optimized by using parallel synthesizers. By utilizing the optimized conditions, 87-membered library of α-iminocarboxamide was successfully synthesized. Next, we have investigated one-pot three-component coupling approach. To our delight, the one-pot three-component coupling reaction of alkyl samarium (III) with isocyanide and isocyanate afforded α-iminocarboxamides in excellent yields.

We also investigated ethylene polymerization and copolymerization activities of α-iminocarboxamide-nickel complexes by using the synthesized ligands. Nickel catalysts were prepared from synthesized a-iminocarboxamides according to a previously reported procedure, after some modification. The crude catalysts were used for the evaluation of polymerization activities of alkenes, without further purification for the sake of throughput improvement. Activities of the prepared catalysts for ethylene polymerization and copolymerization were efficiently evaluated by using a parallel synthesizer.

Keywords: *Combinatorial Chemistry; a-Iminocarboxamide-Nickel(II) Catalyst; Lab-Automation; Multi-component Reaction;*

P-0931

MONODISPERSE LINEAR OLIGOMERS OF UP TO 38 NM LENGTH

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Conjugated shape-persistent arylene-alkynylene oligomers are discussed as one-dimensional molecular wires and as building blocks for supramolecular materials as well as for two-dimensional adlayers on surfaces.[1] Dodecyl-substituted *p*-phenylene-butadiynylene tetramers are obtained via stepwise synthesis using the polar 3-cyanopropyl diisopropyl silyl protective group. Statistical oligomerization under Glaser coupling conditions of the deprotected tetramer and subsequent recycling gel permeation chromatography for separation of the crude products allow an efficient access to monodisperse oligomers of distinct oligomerization degree in sufficient quantities.

Here we present an approach towards monodisperse shape-persistent oligo(phenylene-butadiynylene)s of up to 38 nm length. Self-assembled monolayers of these molecules at the liquid/solid interface (here: 1,2,4-trichlorobenzene/HOPG) are investigated by scanning tunneling microscopy. We also determined the conversion factors for GPC calibration (PS vs. OPB). The overestimation of molar masses of the dodecyl substituted oligomers is unexpectedly lower as compared to the previously investigated hexyl substituted analoga.[1]

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Keywords: *nanostructures; molecular electronics; oligomerization; interfaces;*

P-0932

SHAPE-PERSISTENT MACROCYCLES

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The construction of nanostructured materials with advanced functions from well-designed molecular building blocks is one of the key topics in modern materials chemistry. The shape-persistent macrocycles attract a wide attention of many organic as well as materials chemists, particularly in the last decade, as the molecules, which can be used as building modules for construction of more complex molecular or supramolecular structures with high level of complexity. The “shape persistence” means that the macrocycles are constructed from parts that are rather rigid and connected in such a manner that prevents collapsing of the final structure. In other words, the rigid molecular backbone surrounds an internal cavity which diameter is approximately equal to the backbone length divided by π.

One of the most popular backbones is the arylene ethynylene one, in which the arylene units are connected by ethynylene or diethynylene linkers. For this kind of backbones, many coupling reactions involving ethynyl group were adapted including Sonogashira, Negishi, Heck, Castro-Stephens, and Glaser coupling reactions as well as alkyne metathesis. The last one differs from the others in a possibility of the thermodynamic control of the ring closure reaction. Similarly, the thermodynamic control is possible in construction of the backbones involving annular heteroatoms by imine and amide condensation reactions.

As the backbone consists mostly of π-conjugated segments the pi-pi stacking dominates the intermolecular interactions that result in a remarkable tendency of such molecules to self-organize in 1D, 2D or 3D scaffoldings.

We would like to report on the new shape persistent macrocycles of arylene ethynylene type and of a triangular as well as rectangular shape. Their structure is based on phenanthrene and carbazole units grafted with alkyl chains for better solubility. Their dominant π stacking interaction is in some of them perturbated by incorporation of bulky σ non-congugated units of bicyclo[1.1.1]pentane cages.

Keywords: *Alkynes; Cross-coupling; Macrocycles; Pi interactions;*

P-0933

DESIGN OF NEW BORANES: BROADENING THE SCOPE OF FRUSTRATED LEWIS PAIRS

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Metal-free catalysis is one of the most developing topics in chemistry. The group of Stephan has recently introduced the concept of Frustrated Lewis Pair (FLP), which seems to be a powerful tool in the activation of small molecules, such as hydrogen.[1] Frustrated Lewis Pairs consist of a sterically crowded borane, as the Lewis acid component, and a phosphorous- or nitrogen-containing base that are unable to form stable, classical donor-acceptor adducts. Despite the steric hindrance it is proposed that these pairs associate giving the unique “frustrated complexes”.[2]

The most common Lewis acid that is used for the FLP-based activation of hydrogen is tris(pentafluorophenyl)borane. Despite its availability the application of this borane is limited in the field of Frustrated Lewis Pairs due to its low selectivity. Because of the strong Lewis acidity and the steric accessibility of this boron compound only bulky substrates were capable for hydrogenation.

Based on our previous results[3] we have started to design and synthesize new boranes that are sterically more crowded. We now present the synthesis of some new boron compounds that are promising prototypes of new catalysts.

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Keywords: *borane;*

P-0934

CHIRAL 4,12- AND 4,15- DISUBSTITUTED [2.2]PARACYCLOPHANES

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Our group is interested in the stereoselective formation of supramolecular aggregates. One important element of these is a central dissymmetric unit. So far, BINOL and Tröger’s base derivatives[1] have been proven to be effective for this purpose. Now, we are looking for other types of molecules with uncommon stereogenic elements. One interesting class of compounds in this respect are planar chiral disubstituted [2.2]paracyclophanes[2]. Yet, we have been able to synthesize some disubstituted [2.2]paracyclophanes which can be used as precursor for supramolecular ligands. Most of these difunctionalized [2.2]paracyclophanes are already known[3, 4, 5] but we were able to improve some of the syntheses resulting in higher yields. The key step for the synthesis of enantiomerically pure ligands, however, is the resolution of the enantiomers. In fact, the separation of the paracyclophanes has only been achieved via formation and separation of diastereomeric derivatives obtained upon transformation with optically pure auxiliaries or by enzymatic separation[6, 7, 8]. We now present complimentary methods employing HPLC on a chiral stationary phase that allowed us to improve the resolution of the chiral [2.2]paracyclophanes with regard to yield and optical purity.

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P-0935

MACROCYCLIC NANOCHANNELS AS HOSTS FOR FULLERENE DERIVATIVES

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The formation of channels on a molecular scale is mandatory within living organism, like for example the connection of different compartments such as transmembrane proteins which function as ion channels, transporters or antibiotics. Inspired by the functionality of natural systems, the investigation of self-assembled channel-forming structures has been started to get applied, expanded and adapted. Macrocyclic systems offer the ability to form supramolecular channels if they are organized in a columnar mesophase with close-packing of successive rings. The possibility of inclusion and manipulation of nano-objects becomes feasible depending on the macrocycles' functionalization.[1]

Phenylene-ethynylene-butydiynylene macrocycles containing benzodithiophene units were obtained by the statistical Glaser coupling of the appropriate "half-rings" under Pd catalysis and subsequent purification by recycling gel permeation chromatography. The macrocycles include a nanoscale interior with a diameter of approximately 1.3 nm and exhibit liquid crystalline phases within a wide temperature range of more than 100 K as studied by optical microscopy (crossed polarizers) and differential scanning calorimetry (DSC).

We investigated the solubility of various fullerene derivatives in these liquid crystalline phases. Furthermore, self-assembled monolayers of the macrocycles and coadsorption with fullerenes on HOPG were investigated by scanning tunneling microscopy (STM) at the solid/liquid interface.

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Keywords: *Fullerenes; Macrocycles; Liquid crystals;*

P-0936

DESIGN, SYNTHESIS, DOCKING STUDIES, AND EVALUATION OF LOSARTAN DERIVATIVES WITH POTENTIAL DUAL ACTIVITY AT ANGIOTENSIN II TYPE 1 RECEPTOR AND PEROXISOME PROLIFERATOR ACTIVATED RECEPTOR GAMMA

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Hypertension, diabetes and metabolic syndrome are important risk factors for cardiovascular morbidity and mortality. Angiotensin II plays an important role in blood pressure regulation and angiotensin II type 1 receptors (AT1) blockers are widely used in the treatment of hypertension. Some, such as telmisartan, and at a lesser degree, losartan, also exhibit activity at the Peroxisome Proliferator Activated Receptor gamma (PPAR-gamma), a nuclear receptor involved in the control of glucose metabolism. This represents a new therapeutic approach for the treatment of hypertension and diabetes, which are often concomitant and difficult to treat by one-target molecules.

In this context, instead of pharmacomodulations on telmisartan (already done by Mizuno *et al*.), we preferably choose to modify the structure of losartan, in order to build-up new PPAR-gamma/AT1 dual molecules. The losartan structure was linked to a 4'-hydroxy-5-benzilidenethizolidinedione moiety, which is found in many PPAR-gamma agonists. Many chemical modulations were done on the resulting molecule, in order to get structure-activity relationships to both targets. In parallel, we realized docking experiments, with the aim of predicting the activities of the compounds.

The molecules were docked into the PPAR-gamma receptor by the Autodock software, using a set of various PPAR-gamma X-ray structures from the Protein Data Bank. In order to validate the method, we first applied this procedure for rosiglitazone, a well-known PPAR-gamma agonist.

In vitro AT1 activity was evaluated by displacement of fluorescent angiotensin II in cells overexpressing AT1 receptors. *In vivo* AT1 antagonistic activity was evaluated in anesthetized normotensive Wistar rats *via* the blunted hypertensive response to acute angiotensin II (10^{-10} mol/kg; intravenously). *In vitro* PPAR-gamma activity was evaluated in MCF-7 cells by co-transfection of $(PPRE)_3$-TK-Luc and hPPAR-gamma vectors.

As a result, many molecules showed *in vitro* potency on AT1 or PPAR-gamma receptors. Furthermore, some exhibited strong *in vivo* antihypertensive activity.

Keywords: *bioorganic chemistry; ligand design; structure-activity relationships;*

P-0937

NITROGEN BRIDGED TRIARYLCARBENIUM SALTS AS PLATFORMS FOR ANION RECOGNITION

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Anions play an important role in many biological and biochemical processes. Therefore, their recognition and sensing by artificial receptors is of great interest in the field of supramolecular chemistry. Despite the special intrinsic properties of anions, which hamper the design of efficient artificial hosts, a lot of novel receptors were presented during the last years.[1–3]

Most of them consist of an aromatic platform and at least one side chain containing hydrogen bond donating functionalities such as urea and thiourea moieties. Previous results in our group show that benzene or calixarenes as core molecules for anion receptors are too small to host larger anions such as carboxylates. Therefore, larger aromatic platforms are desirable. Furthermore, the complexation can be improved by the introduction of charged and/ or electron deficient (poly)aromatics.[4]

In our group these strategies were applied to design receptors based on nitrogen bridged stable organic triarylcarbenium ions for the recognition of different mono- and dicarboxylates. All of them are accessible in a few steps from tris(2,6-dimethoxyphenyl)carbeniumtetrafluoroborate by stepwise reaction with particular amines. Their binding affinities to several organic anions were studied by ^{1}H-NMR titration experiments.[5]

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Keywords: *Supramolecular chemistry; Receptors; Anions;*

P-0938

SYNTHESIS AND CHARACTERISATION OF PYRAZOLIDINE BY OXIDATION OF 1,3-DIAMINOPROPANE

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This work presents a new method for the synthesis of pyrazolidine (PYRZ), hydrazine used in the pharmaceutical and cosmetic industries. The new method uses the Raschig process *via* oxidation of the amine (1,3-diaminopropane) with sodium hypochlorite. The advantages of this new protocol are: low toxicity, low associated cost, high reaction rates, high selectivity and high feasibility for a continuous transposition. A global process was developed involving the characterization of the reaction mechanisms, a kinetic study of all the reactions of formation and degradation, the modelling and finally, the optimization of the synthesis parameters. The synthesis part, which is resting on a kinetic approach, was studied in two steps: first, the identification of the products, their kinetic evolution versus time and the knowledge of the associated mechanisms (products were identified and quantified by UV, HPLC/MS and GC/MS methods); secondly, a detailed study of all formation and degradation rates of reactions in order to know the evolution of the pyrazolidine concentrations as function of the initial reagent concentrations, the pH and the temperature.

Keywords: *hydrazine; Raschig process; Pyrazolidine; kinetics;*

P-0939

SYNTHESIS, STRUCTURE OPTIMIZATION AND ANTIFUNGAL SCREENING OF NOVEL TETRAZOLE RING BEARING ACYL-HYDRAZONES

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Candida albicans is an opportunistic and often deadly pathogen that invades host tissues, undergoes a dimorphic shift, and then grows as a fungal mass in the kidney, heart or brain. It is the fourth leading cause of hospital-acquired infection in the United States and over 95% of AIDS patients suffer from infections by *C. albicans*. Existing antifungals can treat mucosal fungal infections but very few treatments are available for invasive diseases. The current antifungal therapy suffers from drug related toxicity, severe drug resistance, non-optimal pharmacokinetics, and serious drug-drug interactions. Because of all these striking problems, there is a pressing need to develop novel antifungal drugs with higher efficiency, broader spectrum, improved pharmacodynamic profiles and lower toxicity. Azoles are generally fungistatic, and resistance to fluconazole is emerging in several fungal pathogens. In an attempt to find novel azole antifungal agents with improved activity a series of tetrazole ring bearing acylhydrazone derivatives were synthesized and characterized by elemental analysis, IR, ^{1}H NMR, ^{13}C NMR, and mass spectral studies. The compounds were screened for their *in vitro* antifungal activity. The mechanism of their antifungal activity was assessed by studying their effect on the plasma membrane using flow cytometry and determination of the levels of ergosterol, a fungal-specific sterol. Propidium iodide rapidly penetrated a majority of yeast cells when they were treated with the synthesized compounds at concentrations just above MIC, implying that fungicidal activity resulted from extensive lesions of the plasma membrane. Target compounds also caused a considerable reduction in the amount of ergosterol. The results also showed that the presence and position of different substituents on the phenyl ring of the acylhydrazone pendant seem to play a role on the antifungal activity as well as in deciding the fungistatic and fungicidal nature of the compounds.

Keywords: *tetrazole; acylhydrazone; Candida albicans; flow cytometry; ergosterol;*

P-0940

STRUCTURE-BASED DRUG DESIGN EXPLOITING DYNAMIC COMBINATORIAL CHEMISTRY TO IDENTIFY NOVEL INHIBITORS FOR ENDOTHIAPEPSIN

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Dynamic combinatorial chemistry (DCC) offers an efficient and innovative approach to accelerate identification of novel ligands for biological targets. In a dynamic combinatorial library (DCL) of acylhydrazones, the connection bonds between the building blocks (aldehydes and hydrazides) are reversible and continuously being made and broken. The composition of a DCL will respond to the addition of a target protein that selectively binds one or more library members and will extract such member(s) from the DCL.[1]

2Using a protein–ligand co-crystal structure of endothiapepsin, a well-accepted model system for the pepsin-like aspartic proteases that are involved in numerous diseases such as hypertension, amyloid disease, malaria and AIDS,[2] we designed a library of potential inhibitors (acylhydrazones) by structure-based design. We have been using a DCC approach to identify the best binder(s) using a DCL generated from five aldehydes and five hydrazides in ammonium acetate buffer at pH 4.5. Using the nucleophilic catalyst aniline (20 mM), the DCL equilibrated in one day. Upon addition of endothiapepsin, the library member(s) captured as potent protein binders are identified by HPLC and LC-MS.[3] After successful identification of the best ligands, these molecules are synthesized separately and tested for their biological activity using an enzyme-based fluorescence assay.

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Keywords: *Drug Design; Inhibitors; Enzymes;*

P-0941

CATALYTIC CARBONYLATION REACTIONS: VERSATILE TOOLS FOR THE SYNTHESIS OF STEROIDAL CARBOXAMIDE DIMERS AND AMINO ACID DERIVATIVES

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Steroids are biologically active molecules widely found in both plant and animal kingdoms, and play significant roles in biological systems. Therefore, there is huge interest in promote structural modifications on steroidal molecules, since the introduction of different functionalities, such as formyl, amide or amino acid groups, into the steroid skeleton, can render marked changes in their biological activity.[1, 2] Particularly, dimeric steroids represent a class of compounds that have recently attracted attention for their rigid, predictable and inherently asymmetric architecture. Steroid dimers, such as natural cephalostatins, ritterazines and the respective analogues have found remarkable pharmaceutical properties, namely, antimalarial, antineoplastic and cholesterol lowering activities.[3]

Since the early discovery of carbonylation reactions in the presence of *O*- and *N*-nucleophiles, iodoalkenes of various structures have been transformed into α, β-unsaturated carboxamides, through aminocarbonylations.[4] However, the use of diamines as *N*-nucleophiles in such reactions is rather limited and the preparation of dimeric molecules using this synthetic strategy has never been described.

In this communication, we report the first Pd-catalyzed aminocarbonylation reactions involving steroids with iodo-functionality and several diamine nucleophiles, as an efficient tool for the preparation of steroidal carboxamide dimers with unprecedented structures. Herein, we also report the synthesis of formyl-steroid derivatives through Rh-catalyzed hydroformylation of unsaturated steroids, and the respective sequential one-pot derivatization into amino acids, *via* Strecker reaction, followed by acidic hydrolysis of the previous aminonitriles.

Acknowledgments: *The authors thank financial support from Programa Compete and QREN/FEDER/FCT (PTDC/QUI-QUI/112913/2009).*

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Keywords: *Aminocarbonylation; Steroids; Carboxamide dimers; Hydroformylation/Strecker reaction; Amino acids;*

P-0942

BOTTOM-UP SYNTHESIS OF STRUCTURALLY DEFINED AND HUNDRED-NANOMETER-LONG GRAPHENE NANORIBBONS

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Graphene nanoribbons (GNRs) are stripes of graphene and possess band gaps in contrast to zero-band-gap graphene. The electronic properties of GNRs depend on their width and edge structures, which make it highly important to fabricate GNRs with structural precision. Top-down approaches such as lithographic cutting of graphene and longitudinal unzipping of carbon nanotubes cannot produce GNRs of defined lateral structures. We have employed a bottom-up approach utilizing the intramolecular oxidative cyclodehydrogenation of highly twisted polyphenylene precursors, and achieved syntheses of structurally defined GNRs. However, it was hitherto impossible to synthesize GNRs with average length of more than 30 nm with this method. In this study, we aimed at the synthesis of structurally defined and longitudinally extended GNRs, and employed Diels-Alder polymerization, instead of previously used Suzuki and Yamamoto polymerization, for the synthesis of polyphenylene precursors. An *AB*-type monomer based on tetraphenylcyclopentadienone was thus designed and synthesized. Interestingly, the molecular weight of the polyphenylene polymers, resulting from the monomer, could be controlled by changing the concentration and the reaction time, and weight-average molecular weight of up to 600000 g/mol was achieved, corresponding to the resulting GNRs of ca. 600 nm. Subsequently, GNRs were synthesized from thus obtained polyphenylene precursors by cyclodehydrogenation. Characterization by IR and Raman spectroscopies as well as an investigation of a model dimer proved the efficiency of the cyclodehydrogenation in this system and the homogeneity of the GNRs. Thanks to the long alkyl chains attached to the periphery, the GNRs could be dispersed in standard organic solvents such as THF and chlorobenzene, which allowed UV-Vis absorption analysis, solution processing, and STM visualization of individual GNRs. In summary, we achieved the synthesis of structurally defined and hundred-nanometer-long GNRs via Diels-Alder polymerization, which also indicated the suitability of this method for the fabrication of highly homogeneous GNRs.

Keywords: *Graphene; Polycycles; Cycloaddition; Raman spectroscopy; UV/Vis spectroscopy;*

P-0943

APPROACHES TO THE SYNTHESIS OF ACYCLIC AND MACROCYCLIC MULTIURACILS

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Earlier we've shown that pyrimidinophanes (macrocycles containing pyrimidine units) do possess high biological activity, comparable with that of reference drugs, and demonstrate a wide spectrum of antimycobacterial activity. We suggested that a compound, consisting of several "monomeric" pyrimidinophanes linked together in some way, can demonstrate higher activity and/or selectivity.

Herein we present the results of our investigations in the area. We've developed several routes to nanosized structures containing pyrimidinophanes. Among them we've chosen those with the highest yield - we used paraformaldehyde to cross-link the macrocycles containing 6-methyluracil. Another option is to link macrocycles through the functional substitutents in either uracil unit or at the heteroatom. Pyrimidinophanes containing propynyl substituents were cross-linked using azide-alkyne cycloaddition and coupling of acetylenes with copper acetate, in some cases the reactions proceed quantitatively.

The same azide-alkyne cycloaddition was used to obtain another type of oligomeric macrocyclic and acyclic pyrimidine derivatives - dendrimers containing uracil units. Di- and oligoazides (i.e. 1,4-diazidomethylbenzene, 1,3,5-triazidomethyl--2,4,6-triethylbenzene, 1,3-bis(5-azidopentyl)-6-methyluracil etc.) were introduced in the reactions with 1,3-bis(w-bromoalkyl)-5--propynyl-6-methyluracil to obtain first generation dendrimers. Subsequent substitution of bromine atoms for azide groups and consecutive reiteration afforded higher generation dendrimers. Such synthetic approach gives us the possibility to introduce various groups and units into the dendrimer molecule by a simple nucleophilic substitution of terminal bromine atoms, another option for modification is again a "click" reaction of terminal azide groups with a wide range of acetylenes, including 5-propynyluracils.

Alkylation of the dimers and oligomers provided the onium salts which were tested towards a series of bacteria and fungi. We've discovered that the earlier found regularities for the monomers do not work for the dimers and higher molecular weight oligomers.

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Keywords: *uracil; dendrimer; synthesis; pyrimidinophane; oligomeric macrocycles;*

P-0944

THE EFFECTS OF PROTIC SOLVENTS AND STRUCTURE ON THE ELECTRONIC ABSORPTION SPECTRA OF THE ISOMERIC PYRIDINE CARBOXYLIC ACIDS

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The ultraviolet absorption spectra of the carboxyl group of three isomeric pyridine carboxylic acids (picolinic acid, nicotinic acid and isonicotinic acid) were determined in a set of protic solvents in the wavelength range from 200 to 400 nm. In order to analyze the solvent effect on the obtained absorption maxima, the ultraviolet absorption frequencies of the electronic transitions in the carboxylic group of the examined acids were correlated using a total solvatochromic equation of the form $\nu_{max} = v_0 + s\pi^* + a\alpha + b\beta$, where n_{max} is the absorption frequency ($1/\lambda_{max}$), π^* is a measure of the solvent polarity, β represents the scale of solvent hydrogen bond acceptor basicities and α represents the scale of solvent hydrogen bond donor acidities. The correlation of the spectroscopic data was carried out by means of multiple linear regression analysis. The solvent effects on the ultraviolet absorption maximums of the examined acids were discussed.

Keywords: *picolinic acid; nicotinic acid; isonicotinic acid; ultraviolet absorption maximum; protic solvents;*

P-0945

PREPARATION OF SYNDIOTACTIC POLY(VINYL ALCOHOL) MICROSPHERES WITH RADIOPACITY VIA SUSPENSION COPOLYMERIZATION AND SAPONIFICATION

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Introduction: Poly(vinyl alcohol) (PVA) can be synthesized by the saponification of poly(vinyl ester) like poly(vinyl acetate) (PVAc) and poly(vinyl pivalate) (PVPi). There have been some reports on the preparation of monodisperse PVAc and PVPi as precursor for PVA via low temperature suspension polymerization of VAc and PVPi. Stable steady monomer droplets are necessary for obtaining polymer beads with narrow particle size distribution (PSD), and excessive coalescence should be excluded at growth stage. In this work, preparation conditions of syndiotactic PVA microspheres with radiopacity via suspension copolymerization and saponification were investigated.

Experimental: To prepare P(VPi/VAc) microspheres with radiopacity, the suspension copolymerization in the presence of aqueous radiopaque nanoparticles was utilized. Suspension agent was dissolved in water under a nitrogen atmosphere and with constant stirring, in a 500 ml three-neck round bottom flask fitted with a condenser. P(VPi/VAc)/nanoparticles microspheres were slowly added to flask during stirring under a nitrogen atmosphere at a fixed saponification temperature. After the reaction, the reaction mixture was poured into cold water and kept for 1 day to separate and to sink s-PVA/P(VPi/VAc)/nanoparticle microspheres of skin/core structure.

Results and Conclusion: P(VPi/VAc)/nanoparticles microspheres were saponified in heterogeneous system, and then the P(VPi/VAc)/ nanoparticles microspheres were converted to s-PVA/P(VPi/VAc) microspheres of skin/core structure via heterogeneous surface saponification. By increasing of saponification time, skin layer of s-PVA/(VPi/VAc)/nanoparticles microspheres got gradually thicker. Nanoparticles enters between high molecular weight polymer chains and thus the gap between chains widens, and hence alkali solution can permeate easily between polymer chains. P(VPi/VAc)/nanoparticles microspheres were converted into s-PVA/nanoparticles microspheres by heterogeneous surface saponification. Radiopacity of the s-PVA/nanoparticles microspheres was confirmed by CT. It showed that s-PVA/TiO_2 and s-PVA/Ti microspheres have excellent radiopacity.

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Keywords: *Poly(vinyl alcohol); Microspheres; Copolymerization; Nanoparticles; Radiopacity;*

P-0946

SYNTHESIS OF MACROCYCLIC OLIGOPHENYLENES

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The spontaneous formation of self-assembled monolayers (SAMs) on solid surfaces is of high interest in the development of nanoscale organic electronic devices. Complex applications require a sufficiently large distance between the active molecular component and the surface enabling conformational changes and electronic decoupling of the functional units from the substrate. In this context, outstanding purpose is the design of anchor molecules affording a perpendicular functionalization of surfaces.

Recently, our group reported on a convenient synthesis of complex phenyl substituted *p*-phenylene oligomers without the need of common transition metal catalyzed cross-coupling reactions requiring complex protective group strategies. Based on these oligophenylenes, bicyclic components are obtained in very good yields. Recycling gel permeation chromatography (GPC) is used for purification. The novel structure is confirmed by ^1H and ^{13}C NMR spectroscopy, MALDI-TOF-MS and most notably by its X-ray determined crystal structure. The molecules have a planar bicyclic unit with a perpendicular center which seems to be a promising structural unit to reach the purpose of three-dimensional growth on surfaces. Self-assembled monolayers at the solid/liquid interface of phenyloctane (PHO) and highly orientated pyrolytic graphite (HOPG) are investigated by scanning tunneling microscopy (STM). The interaction between the bicyclic structure and the surface is further studied using a model host-guest system by means of ^1H NMR spectroscopy titration experiments.

Keywords: *Aggregation; Pi interactions; Surface chemistry; Self assembly; Adsorption;*

P-0947

PREPARATION AND APPLICATIONS OF DENDRITIC CATALYST

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Dendrimers, hyperbranched and perfectly defined polymers, constitute appealing supports for catalysts. Indeed, they display at least two main potential advantages: the possible recovery and reuse of the nano-sized catalysts and, in some cases, a significant enhancement of the activity compared to the parent monomers.

Here we report the preparation and applications of phosphorous dendrimers decorated either with organocatalysts or with metal-based catalysts. In a first example, diarylprolinol derivatives were grafted at the periphery and the activity of the resulting organocatalysts evaluated in Michael reactions. Besides, dendritic thiazolylphosphines were tested as ligands for palladium in Suzuki couplings and dendritic diketones were associated to copper in *O*-arylation reactions. In a last example, dendrimers decorated with terpyridines were used as ligands for rare-earth in Friedel-Crafts acylations. In each case, the recycling abilities of the dendritic catalysts were explored.

Keywords: *catalysis; dendrimers; organocatalysis; transition metals; rare earths;*

P-0948

UNEXPECTED FORMATION OF N-(1-(2-AROYLHYDRAZONO)ISOINDOLIN-2-YL)BENZAMIDES AND THEIR CONVERSION INTO 1,3,4-OXADIAZOLES

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Reaction between aldehydes and carboxylic acids hydrazides constitutes the main pathway in the synthesis of *N*-acyl-*N'*-arylidene-hydrazines, which are precursors in preparation of heterocyclic compounds such as 1,3,4-oxadiazoles.[1, 2]

1,3-phtaladehyde and 1,4-phthaldehyde react with carboxylic acid hydrazides and generates the corresponding bis-aroylhydrazones.[3, 4] However, 1,2-phthaldehyde was reported to behave differently in reaction with hydrazides.[4]

We describe here the condensation products between 1,2-phthaldehyde and various hydrazides, using different reaction conditions as well as their transformation into 1,3,4-oxadiazoles. The isolated *N*-(1-(2-aroylhydrazono)isoindolin-2-yl)benzamides and 1,3,4-oxadiazoles were fully characterized by NMR spectroscopy and high resolution mass spectrometry, indicating that the compounds are present in solution as a mixture of isomers. The *N*-(1-(2-aroylhydrazono)isoindolin-2-yl)benzamide structure was confirmed by X-ray diffraction.

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Keywords: *1,3,4-oxadiazole; 1,2-phthaldehyde; N-acyl-N'-arylidene-hydrazines;*

P-0949

TOTAL SYNTHESIS OF PANDURATIN A, A DENGUE PROTEASE INHIBITOR

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In recent years dengue fever has become the most common mosquito-borne disease worldwide. It is reported that 40% of the world's population or 2.5 billion people in over 100 countries are at risk of dengue fever. Currently no drugs are in clinical use and a vaccine is yet to be successfully developed.

Panduratin A (**1**) and 4-hydroxypanduratin A (**2**) are cylcohexenyl chalcone derivatives of the panduratin family isolated from *Bosenbergia rotunda*, a member of the ginger family.[1] Both panduratin A (**1**) and 4-hydroxypanduratin A (**2**) have shown competitive inhibition of the dengue virus protease with K_i values of 25 ± 8 and 21 ± 6 μM respectively.[2] Thus these compounds are desirable synthetic targets for further study and testing.

Methodology has been developed enabling the synthesis panduratin A (**1**), 4-hydroxypanduratin A (**2**) and other family members. A regioselectivity study on the key high pressure Diels-Alder reaction has also been completed.

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Keywords: *Natural Products; Cycloaddition;*

P-0950

ONE-POT RHODIUM CATALYSED HYDROFORMYLATION-ARYLATION AND SILYLCYANATION REACTIONS

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Enantiopure aryl alcohols are key structural elements in a large number of pharmacologically active compounds.[1] In this context, the addition of aryl organometallic reagents to aldehydes is an attractive synthetic route to prepare this type of molecules. Therefore, the catalytic hydroformylation reaction is a crucial process to prepare several type of new aldehydes, which can be sequentially transformed into high value products.[2]

In this communication we present optimization studies for sequential rhodium/phosphorus or Rh/NHCs catalysed hydroformylation of olefins,[3] followed by *in situ* aldehyde arylation with boronic acids, using the same catalytic precursor. The effect of the reaction conditions and ligand structure on the activity and selectivity of the sequential transformations will be presented and discussed.

Furthermore, the one pot sequential hydroformylation reaction of olefins catalysed by Rh/P metal complexes followed by transformation of the aldehydes into the chiral cianosilyl derivatives catalysed by new titanium/*bis*-BINOL derivatives complexes will be discussed.

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Keywords: *Hydroformylation; Arylation; Cyanosilylation; Tandem reactions;*

P-0951

THE PREPARATION OF THIN POLYANILINE FILMS BY MEANS OF SCREEN PRINTING

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Currently, the research of new materials attracts a large interest of many scientists and enables also new industrial applications. Very interesting area of these new materials are so called functional polymers. These polymers have some additional properties, which allow them to be applied not only as “plastics” in a form of some three dimensional objects, but also to provide more functions (e.g. electrical conductivity, sensitivity to other compounds, fluorescence, bioactivity, etc.). This work is focused on the study of polymers, which show the electrical conductivity. These polymers are usually called as conducting polymers. The phenomenon of the electrical conductivity by polymers was first reported in 1970’s, and was later awarded by Nobel Prize for Chemistry in 2000. The main groups of conducting polymers are derived from polyacetylene, poly(*p*-phenylene), polythiophene, polyaniline, polypyrrole and poly(*p*-phenylene vinylene). Nowadays, these polymers are considered to be applied especially in the form of thin (flexible) layers which then form electrical devices. These layers can be prepared by means of various techniques (spin-coating, printing, other coating methods). The main advantage of the printing techniques is the possibility of pattering, large area application and high throughput. In this study, the films of polyaniline were prepared by means of the screen-printing technique. The quality of the films was optimized by means of changing the formulation of the prepared colloidal poly(N-vinylpyrrolidone) [poly(1-vinylpyrrolidin-2-one)] stabilized polyaniline dispersions, and also by changing of the printing parameters and conditions. The films were prepared on flexible polyethylene terephthalate transparent foil. The prepared films were further investigated by means of the optical microscopy and electrical measurements and profilometry. The thin layers of the polyaniline were successfully prepared. The thickness of the layers ranged from several hundreds of nanometers to 2 µm. The observed physical effects and properties and morphology of the printed films are discussed.

Keywords: *Polymers; Conducting materials; Colloids; Thin films;*

P-0952

ORGANOCATALYSIS: NEW ACCESS TO PHENYLALANINE DERIVATIVES THROUGH THE ENANTIOSELECTIVE DECARBOXYLATIVE PROTONATION

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The enantioselective synthesis of amino acids is a research area of great interest due to the ubiquity of these small molecules in biologically active products. Recently, our lab has developed an efficient methodology to control the formation of carbon-hydrogen bond by an asymmetric organocatalyzed protonation [1]. In this context, our project aims at developing a versatile access to enantioenriched non-proteogenic phenylalanine derivatives, using enantioselective decarboxylative protonation.

This methodology required first the preparation of racemic functionalized hemimalonic acids using a minimum number of steps from readily availalble starting materials. Then, cinchona alkaloids derivatives as chiral bases triggered the asymmetric decarboxylative protonation of these substrates. Recently, the thioureas analogues of these alkaloids promoted the decarboxylation of cyclic a-aminomalonates [2]. However, a stochiometric amount of base and low temperature/long reaction time were necessary to achieve good enantioselectivivies. This presentation summarizes our efforts to obtain high enantiomeric excess of phenylalanine derivatives using a catalytic amount of a new catalyst family, the squaramides. A comparative (squaramides vs thioureas) and comprehensive study of reaction parameters including the nature of the *N*-protecting group (PG) is underway in the specific case of these acyclic substrates.

Keywords: *organocatalysis; decarboxylation; cinchona alkaloids; squaramide; amino acids;*

P-0953

OHMIC HEATING: A NEW AND HIGHLY EFFICIENT PROCESS FOR ORGANIC SYNTHESIS IN WATER

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Synthetic chemists are challenged to consider more eco-friendly and sustainable processes for the generation of the desired target molecules, with reduced energetic impact of transformations mainly for those employed at a production scale. Another challenge of current chemical industry is reducing the use of toxic organic solvents. In this context, chemical reactions in aqueous media arouse great interest because water is non-toxic, non-flammable and relatively available at low cost.

Here we present a new, highly efficient and safe process for organic synthesis in water based on an ohmic heating reactor. Ohmic heating is an advanced thermal processing method where the reaction mixture, is heated by passing electricity through it.[1] Four representative organic reactions, including Diels-Alder cycloadditions, nucleophilic substitutions, *N*-alkylations and Suzuki reaction were performed using this process. The results pointed that ohmic heating allows faster and uniform heating, leading to substantial savings of time with higher yields.

The simple design and cost of the reactor, its easy maintenance and handling, the low heat capacity and thermal inertia of the ohmic heating process, the fast and uniform heating, as well as the possibility of visual monitorization and addition of reagents during the reaction, make the use of this process a highly advantageous and versatile option for organic synthesis especially in water. Thus, the scaling of direct ohmic heating for the pilot scale or even industrial scale should not present the limitations and difficulties of microwave radiation. Therefore, we believe this process is economically viable and environmentally sustainable.

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Keywords: *Sustainable Chemistry; Water Chemistry; Microwave Chemistry; Industrial Chemistry;*

P-0954

IDENTIFICATION OF NEW GABAA RECEPTOR LIGANDS DERIVED FROM VALERENIC ACID

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Root extracts of *Valeriana officinalis* are long used in traditional medicine for inducing sleep and treatment of panic disorders. Valerenic acid, a chiral bicyclic sesquiterpenoidal structure, was found to act as a subtype selective positive allosteric modulator of $GABA_A$ receptors bearing β2 or β3 subunits.[1] Therefore it is mainly responsible for the desirable activity of valerian.

The synthesis of valerenic acid requires exact control of 3 stereocenters and the use of the cost-intensive Crabtree's catalyst. Thus, a simplified scaffold for the design of drugable compounds shall be identified. To this end, the activity related structural motifs need to be discovered by both chemical synthesis and computational methods

We present a comprehensive 3D QSAR model based on a congeneric dataset of 42 valerenic acid derivatives. The atom based 3D QSAR function implemented in Phase/Schrödinger was used. Alignment of training- and test- set- compounds was done in MOE2011.10 based on the best fitting conformation found for the most active compounds. The diaxial arrangement of both onring substituents, found in the X-ray structure of valerenic acid, was chosen as a starting point. The original dataset was randomly divided into 80% training and 20% test set multiple times and the best performing model was chosen to make predictions within a small dataset of related structures. New derivatives were predicted with a R^2 of 0.87 and a Q^2 of 0.73. The quality of the model was tested via biological testing of synthesized compounds.

Acknowledgement: *This work is kindly financed by the FWF project Nr. W1232 Molecular Drug Targets*

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Keywords: *Computational chemistry; Structure-activity realtionships; Ion channels;*

P-0955

A STUDY OF 2-SUBSTITUTED 3,1-BENZOXAZIN-4-ONES

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Substituted 3,1-benzoxazin-4-ones possess interesting biochemical properties including antifungal[1] and serine protease inhibitory[2–4] effects. Some of them are used as ultraviolet absorbers[5] and as acylating reagents or precursors of various heterocycles in organic synthesis[6].

This paper describes our work concerning the preparation of novel benzoxazinones substituted with indole moiety or acyl in position 2. Their preparation is achieved by cyclodehydration of the appropriate *N*-acylanthranilic acids by means of acetic anhydride or thionyl chloride, which is consistent with the standard procedure.

In addition, a new route to starting *N*-acylanthranilic acids has been established. Firstly, *N*-(α-ketoacyl)anthranilic acids were readily obtained from 4-hydroxyquinolin-2-ones by two-step oxidation including peracetic acid hydroxylation into the corresponding 3-hydroxyquinoline-2,4-diones and subsequent oxidative ring opening with periodic acid or sodium periodate. In the cases of the prepation of the mentioned indole derivatives, the appropriate transformations of α-ketoacyl chain were carried out by known chemistry.

As a part of our continued interest in the reactivity of various heterocyclic systems, we have studied reactions of title compounds with some nucleophiles. All compounds under investigation were characterized by available methods of structural analysis including high resolution mass spectrometry and two-dimensional NMR techniques.

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Keywords: *1,3-benzoxazin-4-one; anthranilic acid; cyclodehydration; periodic acid; heterocyclic;*

P-0956

PARA HYDROGEN INDUCED POLARIZATION IN FLUOROUS AND ORGANIC PHASES

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Since the discoveryof the Para Hydrogen Induced Polarization (PHIP) method[1–3] a lotof efforts have been put to develop this technique for practical andcommercial applications in the medicine and the industry[4, 5]. However, there are still some problems which hamper the PHIPutilization. For example, the problem of fast product/catalystseparation is one of special concern[6, 7].

In thispresentation this problem is addressed. We demonstrate that the PHIPeffect can be observed in different fluorous solvents.Further, we present that the PHIP signal can be observed influorous/organic systems. These systems are homogenous at hightemperature and biphasic at low temperature. This temperaturebehavior of fluorous/organic phases can be of crucial importance forproduct/catalyst separation in PHIP.

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Keywords: *Para hydrogen induced polarization; Para hydrogen; NMR; Signal enhancement;*

P-0957

WATER-SOLUBLE N-TYPE CONJUGATED POLYMERS: SYNTHESES AND APPLICATIONS

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N-type conjugated polymers with high electron affinities and high ionization potentials are avidly sought after in the field of organic electronics. In particular, polymer photovoltaic devices frequently comprise fullerene-based acceptor molecules, which are notoriously poor light absorbers in the visible range. Hence, there is a critical need for new n-type polymeric materials.

Here we report the syntheses, characterizations and some potential applications of a series of aqueous-solution processable n-type conjugated polymers. First, the monomeric unit, based on a 1,4-bis(5-bromopyridin-2-yl)benzene skeleton, is conveniently obtained in two steps from commercially available starting materials. This monomer can polymerize under Yamamoto conditions to obtain a poly(pyridine phenylene) precursor, that can undergo post-polymerization conversion into a poly(pyridinium phenylene), water-soluble and electron-deficient polymer. A variety of co-polymers could be obtained following the same synthetic pathway, in order to modulate the optical and electronic properties of the compounds. These materials were found to be moderately soluble in aqueous solutions, and were characterized by ^{1}H NMR, gel permeation chromatography, as well as optical and electrochemical methods. In addition to interesting solubility properties, the polymers were found to possess promising electronic properties, such as reversible redox behaviors, high electron affinities and useful ionization potentials.

Taking advantage of these properties, a variety of applications were envisioned, such as solution-based sensing of electron-rich analytes or enzyme-based electrocatalyis for renewable energy purposes.

In conclusion, we report promising, easily accessible n-type polymers. These materials can be processed in aqueous solutions, display high electron affinities and reversible redox behaviors. These properties make these compounds promising for applications in various fields such as electrocatalysis, sensing or organic photovoltaics, which are currently under investigation in our laboratory.

Keywords: *polymers; electron-deficient compounds; block copolymers; redox chemistry; sensors;*

P-0958

SYNTHESIS OF AN ARTIFICIAL C-NUCLEOTIDE AS PRECURSOR OF TODAY'S NUCLEOTIDES AND THE THERMODYNAMICS OF ITS MOLECULAR INTERACTIONS

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DNA with its four building blocks **A**, **C**, **G**, and **T** is the carrier of genetic information in all known living organisms, no matter how different they are. From which precursor did these nucleotides develop? This is a fundamental question in origin of live science.

A pre-biotic DNA alphabet consisting of only pyrimidine bases has been proposed. This alphabet contains the natural nucleosides **C** and **U** as well as a nucleoside (**D**) which is modelled on 2,4-diaminopyrimidine. **D** can easily form **C** and **U** by hydrolysis and could therefore be their prebiotic precursor.

To investigate this hypothesis, *C*-nucleoside **D** has been synthesised and incorporated into oligonucleotides. Now, isothermal titration calorimetry (ITC) experiments are conducted to probe the thermodynamics of the molecular interactions between **D** and the natural nucleotides.

P-0959

PREPARATION OF 3-THIOURENIDO-2-INDOLONES AND 2-THIOXOIMIDAZO[4,5-C]QUINOLIN-4-ONES FROM 3-HYDROXYQUINOLINE-2,4-DIONES

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3-Aminoquinoline-2,4-diones, accessible by amination of 3-chloroquinoline-2,4-diones,[1] reacts with in situ generated isothiocyanic acid to give mainly 3-thiourenido-2-indolones. 3-Benzyl derivatives of 3-aminoquinoline-2,4-diones yield 2-thioxoimidazo[4,5-c]quinolin-4-ones.[2, 3]

These interesting results gave us incentive to perform analogous reactions with 3-hydroxyquinoline-2,4-diones, which are obtainable by oxidation of 4-hydroxyquinoline-2-ones.[4] Our intention was to prepare oxa-analogues of thioxoimidazoquinolinones and thiourenidoindolones. However, no reaction was observed when a model compound 1-methyl-3-hydroxy-3-phenylquinoline-2,4-dione was boiled with potassium thiocyanate.

On the other hand, 3-(3'-benzoylthioureido)-1-methyl-2--oxo-2,3-dihydro-1H-indole was isolated when KSCN was substituted by NH_4SCN. The same results were obtained with another 3-hydroxyquinolinediones (R_1 and R_2 = Me, Bu, Ph). In addition, using starting compound 3-hydroxyquinolinediones bearing a benzyl group in position 3, C-debenzylation under formation of thioxoimidazoquinolinones was observed.

The exhaustive results will be discussed and the reaction mechanism will be proposed.

Acknowledgement: *This study was supported by the internal grant of TBU in Zlín No. IGA//FT/2012/015 funded from the resources of specific university research.*

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Keywords: *quinoline-2,4-diones; isothiocyanic acid; 3-aminoquinoline-2,4-diones; 3-hydroxyquinoline-2,4-diones; C-debenzylation;*

P-0960

PRODUCTIVITY ENHANCEMENT OF C=C BIOREDUCTIONS BY COUPLING THE IN SITU SUBSTRATE FEEDING PRODUCT REMOVAL TECHNOLOGY WITH ISOLATED ENZYMES

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The bioreduction of C=C double bond of prochiral aldehydes is an important synthetic tool for the generation of optically pure synthones. The first examples of such a reaction were carried out using resting cells of Saccharomyces cerevisiae.[1] In the last decade, great improvement, in terms of conversion and simplicity of work-up, has been achieved using isolated enoate reductases (ERs), such as the Old Yellow Enzymes (OYEs), instead of the whole microorganism. However, the productivity of these reactions is generally low, mainly due to the low substrate concentration used in most experimental set-ups. In addition, the products of isolated ERs-catalyzed reactions are saturated aldehydes which are intrinsically unstable compounds.[2] Here we describe the combination of multienzymatic systems, comprising selected OYEs and alcohol dehydrogenases (ADHs), with the SFPR (in situ Substrate Feeding Product Removal) concept. When applied to the reduction of a set of different prochiral α,β-unsaturated aldehydes to the corresponding saturated products (e.g. some important synthons for the preparation of the bioactive molecules Robalzotan and Rotigotine), this strategy allows an average 100-fold improvement of productivity and helps to preserve the optical purity of products and the chemical stability of reagents. We also observed a remarkable chemoselectivity of selected ADHs toward saturated aldehydes in the presence of α,β-unsaturated aldehydes.[3]

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Keywords: *Biocatalysis; Reduction;*

P-0961

TETRAHYDRO-SS-CARBOLINE-BASED SPIROCYCLIC LACTAM AS POTENTIAL TYPE II' SS-TURN SOMATOSTATINE MIMETIC

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The development of privileged molecular scaffolds efficiently mimicking reverse turn motifs has attracted remarkable interest when structural constraints are exploited to increase both binding and selectivity of model peptides. One of the successful approaches to restrict peptide conformation is the disubstitution in the a position of an a-amino acid, leading to a conformational constraint and a stereochemically stable quaternary carbon center. In particular, spirocyclic scaffolds are able to provide, upon the attachment of appropriate functional groups, useful high-affinity ligands, relevant to the field of drug discovery.[1]

At present, we are interested to spirocyclic tryptophan (Trp) analogues, in order to develop new reverse turn nucleating moieties able to be inserted into pharmacologically relevant peptidomimetic compounds. Among peptides sharing a tryptophan-containing β-turn motif of which the Trp residue is critical for binding, we looked at the hormone peptide somatostatin,[2] acting in various organ systems as a neuromodulator and a neurotransmitter, as well as a potent inhibitor of various secretory processes and cell proliferation.[3] Somatostatin and its analogue octreotide (*Sandostatin*® drug, clinically used for the treatment of endocrine tumors and acromegaly) are thought to interact with the sst1-5 receptors mainly by inserting a β-turn substructure, carrying a lysine (Lys) and a Trp side chain into a pocket of the G protein-coupled somatostatin receptor.

We report here the preparation and structural characterization of a new 1,2,3,4-tetrahydro-β-carboline (THBC)-based spirocyclic lactam as type-II' β-turn model compound and the application of its core structure to the synthesis of a somatostatin mimetic, whose biological evaluation is under way.

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Keywords: *Conformation analysis; Peptidomimetics; Drug design;*

P-0962

SWEET TASTE INVESTIGATIONS ON ASPARTAME AND NEOTAME USING NMR SPECTROSCOPY AND COMPUTATIONAL METHODS

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Aspartame (*N*-(L-α-Aspartyl)-L-phenylalanine,1-methyl ester) is used as an artificial, non-saccharide sweetener in the pharmaceutical and food industry and it is a dipeptide of aspartic acid and phenylalanine.[1] Neotame ((3*S*)-3-(3,3-Dimethylbutylamino)--4-[[(2*S*)-1-methoxy-1-oxo-3-phenylpropan-2-yl]amino]-4-oxobutanoic acid) is a nonnutritive sweetener which is a derivative of aspartame. It is a high-potency sweetener which is 6000–10 000 times sweeter than sucrose and 30-60 times sweeter than aspartame.[2]

The aim of this research is to determine the relationship between structure and taste for aspartame and neotame by using NMR spectroscopy. Assignment of molecules are done by using 1D ^{1}H and ^{13}C, 2D homonuclear NOESY, TOCSY, and 2D heteronuclear HSQC NMR spectra. Molecular interactions of aspartame and neotame within cyclodextrin complexes are investigated and findings are compared with the results that are acquired from computational methods. Although aspartame and neotame have similar structures, they have different taste quality. 3,3-dimethylbutyl group of neotame is the most efficient substituent that makes the difference in taste.[2]

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Keywords: *Nmr Spectroscopy; Cyclodextrin complexes; Computational methods; Aspartame; Neotame;*

P-0963

STUDY ON THERMAL DECOMPOSITION OF P-TERT-BUTYL CALIX[6]ARENE DERIVATIVES WITH DIFFERENT DONOR GROUP AT THE “NARROW RIM” FOR METALLIC IONS EXTRACTION

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Calix[n]arene are cyclic molecules made of some phenolic units *meta* linked by methylene bridges. Owing to their cavity-shaped architecture, they are useful building blocks in the synthesis of receptors for cations, anions and neutral molecules [1]. Calix[n]arene derivatives can be synthesized by modification at the phenol OH groups (narrow rim) and in the *para*-position of the phenyl rings (wide rim).

Calix[n]arene derivatives with ionophoric functional groups at the “narrow rim” exhibit excellent extraction/co-ordination abilities for metallic ions of technological interest. In order to find efficient extracting reagents for precious or rare earth metals, calix[6]arene derivatives functionalized at the narrow rim with three ethylester, three N,N-diethylacetamido, three crotyl, three crotyl-three N,N-diethylacetamido and three crotyl-three ethylester groups were investigated.

The purpose of this study is to investigate the thermal behaviour of the *p-tert*-butyl calix[6]arene derivatives with different donor group at the “narrow rim”. The thermal decomposition was investigated by means of the thermogravimetric (TG) and differential thermogravimetic (DTG) analysis, and differential scanning calorimetry (DSC)[2]. The thermal stability domains, the composition of the pyrolysis products and the thermal effects were determined, on the basis of TG, DTG and DSC plots registered in nitrogen flow. Attempts to analyze the evolved gases using TG-FTIR coupling were also performed.

It was demonstrated that the stability of the *p-tert*-butyl calix[6]arene derivatives depends on both the type and the number of the substituting groups grafted on the calix[6]arene skeleton. The thermal stability data complete the characteristics tableau of the calixarene-based compounds synthesized for the metal sequestration.

Acknowledgement: *This work was possible with the financial support of POSDRU 89/1.5/S/60189 Programme.*

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Keywords: *p-tert-butyl calix[6]arene derivatives; thermal analysis; evolved gas analysis;*

P-0964

ESTIMATION OF KINETICS PARAMETERS FOR IONIC GELATION OF POLYACRYLAMIDE IN DIFFERENT MEDIA

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Polyacrylamide-based hydrogels are used in many water shut -off treatments. Gelation time has the most important effect on polymer gel injection as the controller of the gel placement in porous media. The viscosity of the gelling solution builds up, as the gel network starts forming. So gelation reaction could be studied with viscosity measurements. In this research, sulfonated polyacrylamide was crosslinked with chromium triacetate. The kinetics parameters of the gelation reaction in different media such as distilled water, sea water, formation water and water contained of 10,000 ppm NaCl solution were obtained by steady shear viscometry mesearments. Avrami equation was used to obtain the reaction rate constant and reaction order. The effect of temperature on reaction rate was also investigated the reaction constant which was found to be k=9.3E+15 exp (-10244/T) with an activation energy of 85.17 KJ/mol for distilled water. It was also found that the highest and the lowest order of the reaction was 4.79 and 1.96 for distilled water and for sea water, respectively. This is due to the presence of monovalent and/or divalent ions in the gelant solution which reduced the reaction rate of the gelation with consequent increase of gelation time.

Keywords: *Hydrogels; Kinetics Parameters; Avrami Equation; Reaction Rate Constant; Reaction Order;*

P-0965

BIOCONJUGATION THROUGH MILD AND SELECTIVE NUCLEOPHILIC SUBSTITUTION OF ALCOHOLS "ON WATER"

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Bioconjugation is an expanding field of research.Novel methods for the mild and site-specific derivatization of biomoleculeshave been developed for applications such as ligand discovery, diseasediagnosis, and high-throughput screening. These powerful methods owe theirexistence to the discovery of chemoselective reactions that enablebioconjugation under physiological conditions. A number of water-compatibleorganic transformations such as nucleophilic additions to carbonyl, 1,3-dipolarcycloadditions, Diels-Alder reactions, olefin cross-metathesis and palladiumcatalysed cross-coupling reactions have been optimized for use withbiomolecular substrates in biological systems. From this perspective, thedirect nucleophilic substitution of an alcohol is attractive as it should yieldwater as the only by-product. However, the activation of alcohols in physiologicallyconditions is a fairly challenging topic.

Wedescribe a particular class of alcohols that can generate stabilized carbocationsin aqueous media through "on water" catalysis and that way react with variousnucleophiles in mild conditions. The thiol group of cysteine residues can beeasily alkylated in these conditions and the reaction shows a completeselectivity in the case of competitive reactions between several amino acidsbearing nucleophilic side chains (tyrosine, tryptophan, serine, aspartic acid).

Allthe alcohols described can be functionalized for further application withoutaffecting their reactivity; they are therefore suitable for bioconjugation.This bioconjugation method is the first one based on the direct S_N1-typenucleophilic substitution of alcohols in aqueous media without the requirementof additional catalysis.

Keywords: *Amino acids; Carbocations; Conjugation; Nucleophilic substitution; Water chemistry;*

P-0966

NEW COVALENT ORGANIC FRAMEWORKS BASED IN PERYLENEDIIMIDE DERIVATIVES

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Design and synthesis of microporous materials such as conjugated microporous polymers (CMPs), metal-organic frameworks (MOFs) or covalent-organic frameworks (COFs) have gained momentum in recent years due to their applications such as gas storage, catalysis, or semiconductors[1–3]. In particular, COFs are an emerging class of nanostructured porous and crystalline materials composed by light elements linked by strong covalent bonds to form 2D or 3D architectures[4].

COFs have received remarkable attention as gas storage materials as a result of their high thermal stability, low density and high surface area. Up to now, the incorporation of photoactive molecules in COFs reticular structures is scarce. From this perspective, perylenediimide (PDI) derivatives are excellent candidates for ligands in COFs due to the unique properties (excellent chemical, thermal, and photo stability).

Here in, we present the preparation and photophysical characterization of a new COF incorporating perylenediimide derivatives as ligands. These new materials will find application as imaging agent or solar cell active material.

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Keywords: *Metal-organic frameworks; Solid-state structures; Dyes/Pigments;*

P-0967

PROPELLER-SHAPED MONOMERS WITH ANTHRACENE BLADES FOR TOPOCHEMICAL SYNTHESIS OF 2D POLYMERS

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We aim at the rational synthesis of 2D polymers, defined as “one monomer unit thick” covalent periodic networks. These new synthetic materials, in contrast to conventional polymers, are not easy to prepare due to the complex chemistry behind it. To achieve the goal, we are exploring a topochemical polymerization approach based on a rational monomer design. Here we present two propeller-shaped monomers bearing anthracene blades. We expect these monomers to form laminar single crystals in which the anthracenes stack face-to-face in each layer. After crystallization of the monomers, photo-irradiation of the laminar crystals can induce the [4+4]-cycloaddition reaction among the stacked anthracenes to directly convert the layers to the corresponding 2D polymers. These are then to be isolated as individual discrete entities by solvent-induced delamination as previously demonstrated in our group. Synthesis of the monomers was performed by employing Sonogashira cross-coupling reactions of readily accessible building blocks.

Keywords: *Crystal engineering; Cycloaddition; Photochemistry; Monolayers;*

P-0968

SYNTHESIS AND ANTIMYCOBACTERIAL EVALUATION OF N-BENZYLPYRAZINE-2-CARBOXAMIDES

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In spite of slowly reducing incidence, tuberculosis (TB) belongs to one of the major causes of bacterial infections and mortality in the world. However, the increasing incidence of resistant mycobacterial stems underlines the need to develop new efficient antituberculars.[10] Pyrazinamide (PZA), an essential component of short-course antituberculosis chemotherapy, is used as a model structure for substances referred in this research project. Various substituted *N*-benzylpyrazine-2-carboxamides were prepared as potential antimycobacterial and herbicidal agents by two step synthesis. Substitution of aromatic ring in benzylamines was based on the experience with analogously substituted *N*-phenylpyrazine-2-carboxamides (already proved to be active).[2]

Prepared compounds were characterized by analytical data and screened for *in vitro* antimycobacterial activity against *Mycobacterium tuberculosis* H37Rv, *M. kansasii* and two different stems of *M. avium*. The compounds were also tested for their photosynthesis-inhibiting activity (PET – the inhibition of photosynthetic electron transport in spinach chloroplasts, *Spinacia oleracea* L.), DCMU (3-(3,4-dichlorophenyl)-1,1-dimethylurea, $IC_{50} = 1.9\ \mu mol.l^{-1}$) was used as standard.

Several of prepared compounds exhibited relatively good antimycobacterial activity against *M. tuberculosis* H37Rv comparable with PZA, e.g. *N*-(3-trifluoromethylbenzyl)pyrazine-2-carboxamide ($MIC = 25\ \mu g.ml^{-1}$). Other compounds were also active against stems resistant to PZA.

Photosynthesis-inhibiting activity of the studied compounds was moderate or low in comparison with DCMU, e.g. 5-*tert*-butyl-*N*-(3-trifluoromethylbenzyl)pyrazine-2-carboxamide ($IC_{50} = 15.6\ \mu mol.l^{-1}$).

Acknowledgement: *This study was supported by the Grant Agency of the Charles University (B-CH/ 710312), by the Ministry of Education, Youth and Sports of the Czech Republic and by the Ministry of Health of Czech Republic (IGA NZ 13346).*

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P-0969

COAXIAL MULTICHROMOPHORIC PHOTOSYSTEMS

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The organization of chromophores is pivotal for the performance of optoelectronic devices.[1] Control of the dyes' positioning offers the possibility to regulate the dye to dye interactions and to tune the optical and electronic properties of the chromophores. In the present work we report the preparation of well-organized multichromophoric coaxial charge-transport architectures consisting of phthalocyanine (Pc) and perylenediimide (PDI). Here, a rationally designed Pc, containing structurally supporting peptide side-chains, hydrazides, polymerizable disulfides and diphosphonate anchoring groups was covalently bound onto an ITO surface. Self-organizing surface-initiated polymerization (SOSIP)[2] was used to build vertically aligned Pc assemblies (*p*-type channel) covalently linked by disulfide bonds. An outer vertical electron-transporting pathway (*n*-type channel) was introduced by Pc hydrazide functionalization with PDI aldehydes.[3] The proposed bottom-up approach allows the preparation of highly organized coaxial double-charge transport architectures which could be used as potential active components in photovoltaic cells.

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P-0970

SYNTHESIS OF NOVEL BENZIMIDAZOLE HYDRAZONE DERIVATIVES AND ITS C-NUCLEOSIDES WITH ANTITUMER ACTIVITY

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2-Methylene (aryl) hydrazinobenzimidazole derivatives **2a-e** was obtained when compound **1** refluxed with each of p-methoxybenzadehyde, p-fluorobenzaldehyde, p-nitrobenzaldehyde[1], acetaldehyde and formaldehyde in presence of ethanol and catalytic amount of piperidine. Also, the triazole derivatives **3a-e** was obtained by stirring compounds **2a-e** with mixture of bromine, glacial acetic acid and acetic anhydride. Heating compound **1** under reflux with 2-acetylthiophene and in the presence of ethanol, afforded compound **4**. In the same way, compound **1** undergoes many consecutive reactions with some monosacharides as D (+)-glucose, D (+)-mannose and D (+)-xylose to afford new acyclic N-nucleosides. On other hand, 2-mercapto benzimidazol was reacted with α-bromo-2',3',4', 6'-tetra-*O*-acetyl-D-gulcose or galactose and furnish derivatives **10a,b**. Also, 2-mercapto benzimidazol was reacted with sugar like as 2-chloroethanol or 3-chloro-1,2-propandiol, it give **11a,b**. All tested compounds have antitumor activity with different percentages.

Keywords: *Hydrazinobenzimidazole; 2-Acetylthiophene; Triazole derivatives; Acyclic N-nucleosides; Antitumor activity;*

P-0971

SULFOXIDE AUXILIARY CONTROLLED SUZUKI TYPE C–C-CROSS COUPLING FOR THE SYNTHESIS OF AXIALLY CHIRAL BIARYL NATURAL PRODUCTS

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Axially chiral compounds are very important not only as ligands in organic syntheses but also as natural products. There are many reports of protocols that provide access to biaryl compounds with a high degree of axial stereocontrol.[1]

The natural products Isoplagiochin C and D are cyclic bis(bibenzyls) which have been isolated from liverworts and are showing remarkable antitumor, antibacterial and antifungal activities. Intriguingly, these compounds offer a non-obvious chirality due to the combination of two biaryl axes, a helical stilbene unit and the ring-strain of the entire molecule.[2] Therefore, the use of chiral conditions for the C–C-cross coupling reaction to construct the stereo-determining axis "A" should give raise to an enantioselective synthesis of the macrocyclic isoplagiochin framework.

We refer syntheses of axially chiral biaryls which can be obtained by an asymmetric (diastereoselective) Suzuki–Miyaura-cross coupling between phenyl boronic esters and an aryl iodide tethered sulfoxide auxiliary in *ortho*-position.[3] These syntheses provide the desired axially chiral biaryls in yields ranging from 51-98%, and with diastereoselectivities in the range 50-98% de employing an asymmetric Suzuki-Miyaura process with $Pd(OAc)_2$ and SPhos or (*R*)-/(*S*)-BINAP as ligands. The further synthesis to Isoplagiochin C or D is based on typical Suzuki, Wittig and McMurry protocols.[4,5]

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Keywords: *Suzuki coupling; axial chirality; biaryls; chiral sulfoxide; natural products;*

P-0972

NANOPATTERNING BY MOLECULAR POLYGONS

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Shape-persistent macrocycles are formed by cyclooligomerization of respective acetylene-terminated building blocks under oxidative coupling conditions and subsequently separated by recycling gel permeation chromatography. Self-assembled monolayers of the monodisperse compounds are investigated by scanning tunneling microscopy at the interface of 1,2,4-trichlorobenzene and highly oriented pyrolytic graphite. The macrocycles ($n>2$) can be viewed as *equilateral molecular polygons* (triangles, squares, pentagons, hexagons) that consist of a rigid backbone and long flexible alkoxy side chains. We particularly focus on dithiophene corner units linked by *p*-phenylene-ethynlene-butadiynylene rods. The length of the latter can be systematically increased, and the related polygon dimensions define the pattern periodicities. Additionally, we investigated mixtures of the polygons and obtained well-ordered mixed monolayers at the graphite surface.

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P-0973

COPPER CATALYZED ARYLATION OF ARYLETHYNYL-PIVILANILIDES VIC C-H ACTIVATION

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Transition metal catalyzed C-H activation is one of the most important synthetic tools in recent organic chemistry. Functionalization of aromatic systems bearing directing groups can be achieved most frequently with palladium or copper catalysts. Beside several coupling partners, diaryl iodonium salts are used as aryl transfer reagents. With the utilization of hypervalent iodine compounds anilides can be functionalized in orto or meta position depending on the applied catalyst. Recently Gaunt discovered the meta selective arylation of anilides with diaryl iodonium salts in the presence of copper.[1]

The poster presentation will discuss our recent results on the functionalization of o-arylethynyl-anilides with diaryl iodonium salts in copper(II)-triflate catalyzed C-H functionalization.

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1. Phipps, R. J. Gaunt, M. J. *Science,* **2009***, 323*, 1593-1597.

Keywords: *C-H activation; copper; Iodine; Aromatic substitution; palladium;*

P-0974

FLUORESCENCE BASED METAL ION DETECTION BY ALKYL/ARYL PYRENYL SULFOXIDES

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Chemosensors are molecules which respond to binding analytes of interest by changes in its colourimetric, photophysical, electrochemical properties. Fluorescence being a very sensitive and non-invasive technique is well suited for chemosensing. Fluorescent chemosensors for ions have been widely used to monitor ions' concentrations in biological, environmental and biomedical assays. Most such fluorionophores are based on signaling mechanisms like photoinduced electron transfer (PET), intramolecular charge transfer(ICT) or binding-induced conformational restriction[1]. Prevention of photoinduced electron transfer by oxidation of sulfoxide to corresponding sulfone has been used to detect oxidant analytes e.g. Triacetone triperoxide (TATP)[2]. Interestingly, oxidation of sulfide to corresponding sulfoxide leads to decrease in fluorescence quantum yield, an observation which cannot be explained by PET quenching[3]. These less fluorescent sulfoxides provide an opportunity to develop fluorescent chemosensors based on fluorescence recovery upon ion binding by the sulfoxide. A series of alkyl/aryl pyrenyl sulfoxide were synthesized and found to exhibit fluorescence enhancement with Zn^{2+} and Li^{+}, and reduction with Fe^{3+} metal ions.

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Keywords: *Chemosensors; Fluorescence; alkyl/aryl pyrenyl sulfoxides;*

P-0975

LEWIS ACID CATALYSED INVERSE ELECTRON-DEMAND DIELS-ALDER REACTION – A NEW SYNTHETIC ENTRY TO STEROIDS

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A highly functionalized cyclopropanated naphthalene is easily accessible in one step via a domino inverse electron-demand Diels-Alder (IEDDA)-cyclopropanation reaction catalysed by a bidentate Lewis acid[1]. This intermediate can be transformed[2] to a precursor ideally suited for a homo-Nazarov cyclization[3] yielding directly the 6-6-6-5-tertacyclic steroid ring system. This strategy provides a straightforward access to steroids, i.e. estrogens as potential anticancer agents, which are difficult to prepare by standard steroid functionalization procedures.

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Keywords: *Synthetic methods; Total synthesis; Steroids;*

P-0976

SYNTHESIS OF PORPHYRIN ESTERS WITH BILE ACIDS

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The goal of this project was to synthesize porphyrin with bile acid. Bile acids are acids derived from cholesterol. Basic bile acid is cholic acid and chenodeoxycholic acid. These acids are very important part of metabolism – they are in bile and make its largest organic ingredient. Bile acids have an important role in digestion of lipids[1]. The second part of synthesized molecules was porphyrin. Porphyrins are cyclic organic substances derived from tetrapyrrol of porphyn. They make basis of huge number of important substances like heme, vitamin B12 and chlorophyll[2]. Substances similar to these which we prepared may be used in pharmacy.

We have prepared the derivate of porphyrin from commercially obtained meso-(tetrahydroxyphenyl)porphyrin by successful synthesis with lithocholic and cholic acid. Esterification proceeded in DMF with chemical reagent EDAC or HOBt. Porphyrin synthesized with cholic acid was thereafter metalized by ions of gadolinium, cooper, nickel or zinc.

Every synthesized substance was characterized by NMR, mass, infrared and UV-VIS spectroscopy. Measurements proved successful synthesis of substances and pointed out to other different properties.

Planed synthesis of six substances unknown to date and their characterization was successful. In case of substance **2**, there were aggregation studies made in different proportion DMSO : H_2O which indicate the likely properties of heteroaggregation.[3]

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Keywords: *Porphyrinoids; Steroids; Metalation;*

P-0977

MASS SPECTROMETRIC INVESTIGATION OF RUTHENIUM CATALYSED REACTIONS

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Transition metal catalysts have occupied the central role in most carbon-carbon bond-formation reactions in context of selectivity (chemo-, regio-, diastereo and enantioselectivity) and atom economy. Compared to other transition metals, ruthenium has the widest scope of oxidation states (from -2 valent to octavalent) and various coordination geometries in each electron configuration. This led to an increased use of ruthenium catalysts in numbers of reactions.[1, 2] According to these universal properties there is a need to deeply explore the reaction mechanisms to discover and understand the great potential of this metal.

Binding energies of ruthenium complex $RuCp(CH_3CN)_3PF_6$ have been studied by mass spectrometry using collision induced dissociation with xenon and ligand exchange interactions with unsaturated hydrocarbons. Reaction intermediates have been investigated by spectroscopic measurements using infrared multiphoton dissociation spectroscopy.[3] Experimental measurements have been compared with quantum chemistry calculations using density functional theory methods.

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Keywords: *Ruthenium; Mass spectrometry; IR spectroscopy; Density functional calculations;*

P-0978

PREPARATION OF PORPHYRIN-BASED HPLC COLUMNS FOR THE SEPARATION OF FULLERENES

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Because of their interesting properties fullerenes are very attractive compounds both for the industry and for the basic research. Their massive applications are still restricted due to their high price, which is a consequence of very complicated separation from the crude fullerite soot. It is known that fullerenes can interact with porphyrin moieties, especially if they are preorganised in suitable geometry. We prepared some HPLC columns based on 5,10,15,20-(*p*-aminophenyl)porhyrin and his metallated derivatives anchored on silica gel. These columns were used in the separation of fullerene mixtures by HPLC under different conditions and the results were compared with those of commercial columns designed for fullerene analysis.This research was supported by the Czech Science Foundation (GACR 203/09/0691) and finacial support from specific university research (MSMT No 21/2012).

Keywords: *Fullerenes; Separation; Porphyrin; Chromatography;*

P-0979

UNPRECEDENTED META-SUBSTITUTION OF CALIXARENS: DIRECT WAY TO INHERENTLY CHIRAL RECEPTORS

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The electrophilic aromatic substitution in calix[n]arene series is a well-established procedure leading exclusively to the *para*-substituted derivatives. Here, we describe an unprecedented regioselectivity of mercuration reaction leading to the *meta*-substituted calix[4]arenes. We have recently described similar unexpected regioselectivity during the nitration and formylation of thiacalix[4]arene[1] skeleton.

These compounds represent a new type of substitution pattern in classical calixarene chemistry and open the door for the straightforward synthesis of inherently chiral receptors based on calixarenes.

Acknowledgement: *This research was supported by the Czech Science Foundation (P207/12/2027).*

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Keywords: *Calix[4]arenes;*

P-0980

BUILDING BLOCKS FOR SUPRAMOLECULAR PHOTOCATALYSIS BASED ON 2,2'-BIBENZIMIDAZOLE

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In natural photosynthesis, light driven electron transfer processes between an oxygen evolving manganese cluster and several reduction catalysts lead to efficient water splitting and fixation of CO_2. In green leafs, the process is powered by light absorption through the porphyrin-moieties of the photosystems P680 and P700. In artificial photosynthesis, tris(bipyridyl)ruthenium(II) complexes have proven their ability to convert light as efficiently into electronic energy to drive chemical conversions. One of the most challenging aspects here is to establish the directional electron transfer between two catalytically active systems. Looking at the electron transfer chain of the z-scheme, guiding the intermolecular transport of an excited electron through supramolecular pre-orientation is an interesting route.[1] Several groups including ourselves have shown that ruthenium(II) chromophors containing a bibenzimidazole ligand establish defined supramolecular assemblies with anions as well as cations through hydrogen bonds.[2–4] Since such aggregation changes the luminescent properties of the complexes, the corresponding complexes can also be considered as luminescent sensors. Following the procedure presented by Siegel et al.[5] we synthesized several substituted bibenzimidazoles and their corresponding ruthenium(II) complexes and characterized them with respect to their photochemistry, also in the presence of several guest molecules.

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Keywords: *Bibenzimidazole; Ruthenium; Photochemistry; Supramolecular;*

P-0981

SYNTHESIS OF TETRAHYDROCHROMENOINDOLE VIA AZACOUMESTANES

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Heterocyclic natural products, particularly indoles play a prominent role in biological systems. A multiplicity of biologically active natural products and agents derive from the indole nucleus, hence a selective synthesis of indole derivatives still is of high interest.[1]

Recently, from the roots of *Robinia pseudoacacia* H. Mohammed isolated a new natural product of the tetrahydrochromenoindole[4,3-*b*] type, which can be considered as the "indole" analogue of the well-known medicarpine. Further research has showed the cytotoxic effect of the compound against human promyelocytical leukemia cells.[2] Therefore, because of its promising properties, a total synthesis of tetrahydrochromenoindoles is worthwhile.

Here, we report on the regioselective synthesis of this heterocyclic structure through Suzuki-Miyaura-coupling between indole boronic esters and adequate substituted arylcarbamates[3] to appropriate indolecarbamates in 71–83% yield. Subsequent intermolecular cyclisation provides an azacoumestane as intermediate, which affords the desired natural product by reduction and subsequent hydrogenation.

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Keywords: *heterocycles; indole; natural products; total synthesis;*

P-0983

ELECTRIC-FIELD ASSISTED PHOTOGENERATION IN POLY(N-VINYLCARBAZOLE) DOPED WITH 2,4,7-TRINITROFLUORENONE

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Polymeric photoconductors have many positive characteristics such as wide spectral sensitivity, low cost, and architectural flexibility. Such materials can exhibit high photogeneration efficiency, though in general they show relatively low charge carrier mobility. The polymeric photoconductors known thus far are polymers with a saturated backbone containing active chromophores as pendant groups or molecularly dispersed dopands. Poly(*N*-vinylcarbazole) (PVK), sensitized by adding the electron acceptor 2,4,7-trinitrofluorenone (TNF), is the best known and most widely investigated polymeric charge-transfer (CT) complex system.[1–2]

In this paper we present results of examination of surface voltage photodischarge in PVK+TNF CT system. The samples of PVK, and their CT complexes with TNF were prepared by dissolving them in dichloromethane and by casting them on chromium-plated metal supports at room temperature. For the PVK+TNF system, one can recognize the CT band at around 450 nm.

The photogeneration quantum yield in the obtained nanocomposites were determined by means of Surface Potential Decay method consisting in monitoring of speed of the surface potential decay induced by illumination of the film with different initial surface potential. An HBO-200 mercury lamp with 430 nm interference filter was used as a light source. PVK+TNF films show remarkably dark decay and photodecays of the doped PVK samples are initially very quick. The potential decay rate is proportional to the photogeneration quantum yield of PVK+TNF system.

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Keywords: *Photophysics; Polymers;*

P-0984

CATALYTIC HYDROGENOLYSIS OF CALIXARENE DERIVATIVES

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Tobisu et al. recently published work about selective hydrogenolysis of alkyl(aryl)ethers and arylpivalates using silane and nickel(0) as a catalyst.[1] Using this method on calix[4]arenes can lead to dehydroxylated derivatives in high yield.

First step in the synthetic pathway is creation of derivatives suitable for hydrogenolysis. Due to the presence of silane, all free hydroxy groups have to be modified. Pivalate can be used as a reactive group and rest of the substituents should be unreactive propoxy group. This can lead to several derivatives differing in conformational isomerism, number of reactive pivalates and substituents on upper rim.

These derivatives can undergo hydrogenolysis using the $Ni(cod)_2/PCy_3$ catalytic system and dimethoxymethylsilane as a hydrogenolytic agent. Preliminary results show creation of didehydroxydipropoxycalix[4]arene in low yield.

Another method was recently published by Sergeev and Hartwig.[2] They used *N*-heterocyclic carbene ligands instead of relatively unstable PCy_3. Best results were achieved with 1,3-bis(2,6-diisopropylphenyl)imidazolidinium chloride activated by sodium *terc*-butoxide. Hydrogen was used as the hydrogenolytic agent although silanes can be used as well. Using this system on tetramethoxycalix[4]arene afforded partially hydrogenated products. Reaction optimization should lead to higher yields and afford selectively hydrogenolysed derivatives.

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Keywords: *Calixarenes; Nickel; Carbene ligands; Silanes; Hydrogen;*

P-0985

SYNTHESIS AND STRUCTURAL STUDY OF SUGAR DERIVATIVES OF OLIGOPYRROLES USING CIRCULAR DICHROISM

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Ultraviolet circular dichroism (CD) is a standard mean for determining average secondary structure of many systems. Empirical interpretations of the CD spectra are very often not reliable. Unfortunately, CD is quite a complex phenomenon, and its simulations are currently still restricted by limited computer power and methodology problems[1]. This is unfortunate as CD provides enhanced information not only about molecular structure, but also about molecular interactions comprising solvent or other molecules.

Therefore, combined computational techniques were utilized to provide more reliable representation of the experimental data. The theory was applied for carbohydrate-oligopyrrole condensates. The cyclic oligopyrroles (e.g. calix[4]pyrroles), similarly as porphyrin–carbohydrate conjugates, were found important as sensitizers in the photodynamic therapy. They can also incorporate into cell membranes, and interact with DNA and nucleotides, and exhibit electrochemical properties suitable for catalysis or usage in analytical chemistry. Calix[4]pyrrols were described as anion and neutral binders, chromatic, fluorescent or optical sensors.(e.g. Schell, 1999 or Zhang, 2001).

A single calix[4]pyrrole cycle has zero CD signal. But chiral molecules (even not absorbing in UV-VIS, such as saccharides) can induce measurable CD. The CD signatures were studied with mono- or disubstituted tetrapyrroles. Effect of their aggregation into bigger units were also tried to be studied by concentration dependence.

We aimed our attention to the direct carbohydrate functionalisation of oligopyrrole core via stable *C*-glycosidic bound which mimics well normal *O*-glycosides. This area is very challenging because even when we elarge the scope, cyclic oligopyrroles with carbohydrate substitution the meso-like and β-pyrrolic are rather rare[3].

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Keywords: *Circular dichroism; C-Glycosides; Supramolecular chemistry;*

P-0986

SALT-INDUCED EFFECT UPON THE PROXIMITY BETWEEN THE PYRENE LABELED POLY(ACRYLIC ACID) AND SDS MICELLE

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The effect of salt upon the proximity between the pyrene labeled poly(acrylic acid) (PAAPy) and SDS micelles was studied by steady-state and time-resolved fluorescence spectroscopy. The technique employed was the fluorescence energy resonance transfer (FRET) between naphthalene probe as donor and Py label used as acceptor. We explored the changes at the level of the micellar interface caused by the presence of polyelectrolyte. A significant change of FRET was observed increasing both salt and surfactant concentrations. The donor-acceptor distances were calculated using Förster theory. A minimum donor-acceptor distance was established for a critical salt concentration. The favored interactions that involve SDS binding to PAAPy result from a delicate charge screening effect of Na^+ counterions acting at the micellar interface.

Keywords: *fret; micelles; polymers;*

P-0987

A NEW METHOD FOR THE METALATION OF AZOBENZENES

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The direct metalation of azobenzene often leads to a reduction of the azo group to give hydrazine derivatives as main products instead of the desired metalated azobenzene species.[1] As an example, the maximum yield for the lithiation of azobenzene by halogen metal exchange is around 42 %.[2] Therefore, in cross-coupling reactions with azobenzenes, these compounds always servs as electrophiles (for example the iodinated species) which greatly limits the scope of the reaction. To solve this problem, we have developed a new, fast and easy method to metalate and transmetalate azobenzenes selectively in para and meta position of their aromatic units in high yields. We show that these can be used as reactants in cross-coupling reactions.

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Keywords: *Azo compounds; Lithiation; Transition metals;*

P-0988

NOVEL HETEROARENIUM CATALYSTS FOR SULFOXIDATIONS

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Chemoselective introduction of oxygen into an organic molecule represents one of the key transformations in organic synthesis. Many organocatalysts are capable to introduce oxygen (even stereoselectively) into an organic substrate, e.g. chiral ketones and iminium salts. Among them, flavinium salts seem to be the most promising mediators for sulfoxidations and Baeyer-Villiger oxidations.[1] These catalysts are inspired by natural enzymes, where flavin moiety is present in the active site. In the catalysis of oxidations with hydrogen peroxide, flavinium salts form flavin-hydroperoxide which is the oxidising agent for the substrate. Oxidations of sulfides promoted by flavinium salts are highly chemoselective – no overoxidation to sulfones occurs. Use of chiral flavinium salt results in stereoselective oxidation.[2]

We have found that flavin moiety is not necessary – pyrazinium salts[3] bearing electron-withdrawing substituents form pyrazine-6-hydroperoxides and oxidise substrates in similar manner as flavin catalysts. Major advantage of these salts is easy availability.

This work is focused on heteroarenium salts based on pyrimidine. Effect of both electron-withdrawing and electron-donating groups in position 2- and 4- is examined to determine influence of electronic effects on catalytic cycle. Also effect of alkyl chain length and counteranion was studied to optimize catalyst core for introduction of cyclodextrin moiety and to make oxidations stereoselective.

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Keywords: *organocatalysis; pyrimidine salts; sulfoxidation; organic peroxides;*

P-0989

MOLECULAR SWITCH BASED ON CUCURBITURIL

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Macrocycles cucurbit[*n*]uriles (**CBn**) can create supramolecular complexes with some positivly charced guest. We used as a guest simple lutidine derivative with carboxyalkyl group. We will demonstrated that the lutidine derivative forms stable inclusion complexes with **CB6** and **CB7** at acidic water. Under the complex formation **CB6** engulfs aliphatic part of the guest contrary to **CB7** which bind lutidinium part. Affinity of lutidinium toward **CB6** is weaker compared to **CB7** also the exchange of the guest molecule within the macrocycle take place significantly slower in the former case. Under basic condition the **lutidinium•CB6** complex dissociates while the formation of **lutidinium•CB7** also with smaller value of association constant.

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Keywords: *Receptors; Macrocycles;*

P-0990

SYNTHESIS OF DIARYLKETONES FROM ALDEHYDES AND N-ARYLACETAMIDES VIA PALLADIUM CATALYZED C-H ACTIVATION UNDER MILD AQUEOUS CONDITIONS

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The importance of cross coupling reactions in synthetic organic chemistry is well known. Recently couplings via C-H activation came to the front due to its halogen free, environmentally benign way of create new carbon-carbon bonds. Herein, we present our results on the palladium catalyzed oxidative coupling of substituted N-arylacetamides and benzaldehyde derivatives. This orto directed palladium catalyzed coupling via C-H activation was discovered very recently, however the known procedures require high temperature and organic media. We developed a mild condition to prepare a wide range of N-(2-benzoylphenyl)-acetamides using water as a solvent, at room temperature. The presented conditions allow straightforward transformations in shorter reaction time, and the functionalization of more challenging substrates. Mechanistic investigations are also discussed.

Keywords: *C-H activation; Ketones; Cross-coupling; Palladium; Oxidation;*

P-0991

TWISTED CHIRAL PADDLEWHEEL STRUCTURE: SYNTHESIS AND STRUCTURE DETERMINATION OF DIRHODIUM COMPLEXES BY CHIROPTICAL SPECTROSCOPY

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Dinuclear rhodium complexes are versatile compounds, being currently used as effective catalysts, anticancer agents and building blocks for supramolecular chemistry[1]. We have developed methods for separation and synthesis of tetrakis(carboxylato)dirhodium(II) $[Rh_2(\mu\text{-}O_2CR)_x(\mu\text{-}O_2CCH_3)_{4-x}$ x:1-4] complexes, where the chiral ligands were protected amino acids[2]. Based on our previous work[3] we found that vibrational and electronic circular dichroism spectroscopies are powerful tools for determining the steric structure of chiral complexes. This presentation deals with diastereoselective synthesis and structure elucidation of chiral rhodium complexes where the used ligands are natural and unnatural amino acids and other carboxylic acids. The synthesis is simple, without additional reagents, and water can be used as green solvent. These complexes have non-tipical, twisted paddlewheel structures, because the chiral ligands are coordinated to the Rh_2 unit by bidentate chelating mode. Their steric structure was determined by chiroptical (VCD, ECD) spectroscopy supported by theoretical calculations at *ab initio* (DFT) level of theory. Results of the theoretical calculations on the electronic structure of studied complexes indicate their applicability in catalytic reactions.

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Keywords: *Chiroptical spectroscopy; ECD; VCD; chiral dirhodium complex;*

P-0992

EPIMERS VS. INVERSE EPIMERS: THE ABSOLUTE CONFIGURATION OF ALNUMYCINS

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Alnumycins are aromatic polyketides produced by *Streptomyces* bacteria. They are composed of an isochromanequinone aglycone which is directly linked via a C-C bond to a sugar or a sugar-like unit. The bacterial aromatic polyketides have a number of established medicinal applications including use as antibiotics. Alnumycin A was originally described as a single compound but it was recently found to consist of a set of six stereoisomeric compounds[1]. They were isolated as part of our work elucidating the biogenesis of these compounds[2].

The determination of whether two stereoisomers constitute an epimeric pair or if they differ in their configuration at all stereogenic centers bar one can be a formidable challenge and represent a problem of greater complexity than just determination of absolute configuration *per se*. The latter stereochemical relationship is hereby defined as a pair of inverse epimers and is exemplified by alnumycins A1–3 to introduce the concept[1, 3]. Of these three pairs of naturally occurring C-1 inverse epimers, for the two new ones, alnumycins A2 and A3, the assignment of relative configurations was assigned based on ^{1}H NMR NOE contacts and molecular modeling using density functional theory (DFT). Absolute configurations and inverse epimeric relationships were determined by the use of NMR spectroscopy together with chiral derivatization (MTPA) and by experimental circular dichroism (CD) measurements in conjunction with theoretical calculations.

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Keywords: *Enantioselectivity; Diastereoselectivity; Polyketides; Circular dichroism; NMR spectroscopy;*

P-0993

BRIDGED AZOBENZENES – A NEW GENERATION OF SWITCHES

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Azobenzenes as photochromic switching unit have been used to achieve a number of dynamic molecular functions. Driving directed motion in molecular motors or on surfaces is not possible because the "mechanical" power stroke affected by the *trans-cis*isomerization can point in two directions leading to two enantiomeric *cis* isomers. Randomly directed power strokes would not lead to directed motion.

We therefore designed molecules based on azobenzene units that would perform power strokes preferentially to one direction (leading to diastereomers of different energy). Diazocines (azobenzenes bridged by a CH_2-CH_2 group in *ortho* position) are a good starting point for molecular design because diazocines are superior to azobenzenes with respect to photoconversion and quantum yield.[1] Whereas the parent diazocine still performs isomerization in two directions steric hindrance can be introduced at the CH_2-CH_2 bridge or at the *ortho* positions of the phenyl groups to disfavor one direction.

The final goal is to attach these modified diazocines covalently to molecular platforms[2] and to prepare self-assembled monolayers. Directed motion would be induced by a cilia like movement of the switchable units using polarized light.

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Keywords: *Azo compounds; Diazo compounds; Isomerization;*

P-0994

SUBSTITUTED 5,6-DIHYDRO-4H-PYRROLO[1,2-B]PYRAZOLES

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The pyrazole based natural product - alkaloid withasomnine was isolated from the roots of *Withania somnifera*, *Newbouldia laevis*, the shrub *Elytraria acaulis* and from the stem bark of *Discopodium penninervium*. Beside its analgetic effects, withasomnine has both CNS and circulatory system depressant properties. There are few publications related to the synthesis of this compound.

We report here two synthetic pathways leading to substituted 5,6-dihydro-4*H*-pyrrolo[1,2-*b*] pyrazoles. The first procedure starts with g-butyrolactone, which is transformed to 6-chlorohex-1-en-3-one alternatively in 3 or 5 steps and in following 4 steps we are able to prepare substituted bicyclic compounds. The last step is Suzuki coupling where we tested different conditions changing substituted boronic acids and various Pd-catalysts. The second route comprise thermally initiated intramolecular cyclizations of substituted homoallenyl azines prepared from homoallenyl aldehydes to desired 2,4-disubstituted heterocycles.

Keywords: *withasomnine; pyrrolo[1; 2-b]pyrazoles; Suzuki coupling; homoallenyl azines; intramolecular cyclization;*

P-0995

PYRROLIDINE IMINOSUGARS WITH BIOLOGICAL ACTIVITY

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Pyrrolidine iminosugars are sugar analogs (furanoside form) with the endocyclic oxygen replaced by a nitrogen atom, initially known as potent glycosidase inhibitors. They have also been found to be inhibitors of other glycoprocessing enzymes widening the area of their medical applications (drugs for metabolic disorders, antiviral and anticancer agents). Iminosugars are therefore of growing interest as new therapeutic leads.

Preparation of pyrrolidine iminosugars is challenging, involving multistep procedures with low yields and poor stereoselectivities and this is the reason why there are no systematic studies on the effect of stereochemistry change at the chiral centers in the iminosugar ring. So, new methods are required for fast access to a series of these valuable biologically active compounds with systematic structural or stereochemical changes in order to determine a structure – activity relationship.

The synthesis of pyrrolidine iminosugars by green and more efficient methods involving the use of microwave and/or ultrasonic activation will be presented, as well as the characterization of the synthesized compounds.

The most active iminosugars to be synthesized were identified with the in-house designed QSAR software: PRECLAV (Property Evaluation by Class Variables) based on a calibration set for which the biological activity was reported in literature.

Keywords: *pyrrolidine iminosugars; qsar software;*

P-0996

SYNTHESIS AND PROPERTIES OF NOVEL SEMICONDUCTING DONOR-ACCEPTOR MATERIALS

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In Organic Electronics there is a permanent need for new electron-conducting materials. To that end, an entire series of different acceptors such as fullerenes, phthalocyanines and rylene-type dyes has already been successfully examined.[1] Nitrogen-containing acenes are a class of semiconducting materials which are highly interesting for their application in organic electronics.[2] An exciting extension of this topic is the connection of these acceptors to donor molecules to form π-conjugated oligomeric and polymeric compounds in order to adjust electronic properties and to induce intramolecular and intermolecular interaction, which enhances charge carrier transport.[3]

Herein, we will report on the synthesis of symmetric donor-acceptor-donor systems which can be easily synthesized by Pd-catalyzed cross-coupling. According to DFT-calculations, these materials show a HOMO-LUMO gap that would make them candidates as absorber materials for organic solar cells. Furthermore, the energies of the frontier molecular orbitals seem to make the synthesized compounds capable of serving as semiconductors in OTFTs (organic thin film transistors).

The opto-electronic properties of the oligomers will be examined both in solution and in thin films; their semiconducting properties will be studied in field-effect transistors.

As one aspect of future studies will be printing of these materials, special focus will be on their solubility in non-chlorinated solvents.

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Keywords: *Organic Electronics; Donor-acceptor systems; Electron transport;*

P-0997

MOLECULAR DYADS WITH STRONG PUSH-PULL CHROMOPHORES AS ELECTRON ACCEPTORS: SYNTHESIS AND PHOTOPHYSICAL PROPERTIES

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One of the approaches in the development of organic solar cells (OSCs) is the molecular one, wherein a donor (D) and an acceptor (A) are covalently attached to a bridging unit (B) in a molecular dyad. While impressive progress has been made in OSC development, one of the limiting factors, in particular of covalent D–B–A dyads, has been the restricted set of acceptors used so far, mainly comprising derivatives of fullerenes, perylene diimides, and quinones.

As an alternative to the often used fullerenes, a new class of strong organic electron acceptors (push-pull chromophores) has been introduced by the Diederich group into covalently linked donor-acceptor systems for photoinduced electron transfer (PET). These "superacceptors" are accessible by a versatile [2+2] cycloaddition (CA), between electron-rich alkynes and electron-poor alkenes, e.g. tetracyanoethylene (TCNE), followed by a retro-electrocylization (RE).[1, 2] The superacceptors have been incorporated into covalently linked molecular dyads with a *meso*-*trans*-bis(3,5-di-*tert*-butylphenyl)-zinc-porphyrin as electron donor. The photophysical properties of these molecular dyads and, of according reference compounds have been studied using steady state and time-resolved absorption and luminescence spectroscopies, both as solutions in aerated and deaerated toluene and benzonitrile.

As evidenced by nanosecond transient absorption spectroscopy, the main deactivation pathway for dyad **1** is energy transfer, and electron transfer in the case of dyads **2** and **3**. In benzonitrile, dyad **2** exhibits a long-lived charge-separated state of 2.3 μs. Further studies with this new promising class of acceptors are under way to examine their potential for PET in rigid molecular dyads, and as novel materials for OSCs.

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Keywords: *Molecular electronics; Electron transfer; Energy transfer; Supramolecular chemistry; Porphyrinoids;*

P-0998

SYNTHESIS OF TRICYCLIC INDOLE DERIVATIVES VIA ASYMMETRIC ORGANOCATALYSIS

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Asymmetric organocatalysis is a powerful method to assemble chiral molecules without using transition metals or harsh reaction conditions. Most of the applied organocatalysts have been synthesized from renewable sources (e.g., amino acids, alkaloids) and used in enantio- and diastereoselective syntheses of complex chiral molecules, which are valuable building blocks.

We have developed bifunctional cinchona based thiourea catalysts, which have been used in several asymmetric transformations with high enantioselectivities and yields[1, 2]. Recently, we have applied these bifunctional catalysts in an iterative Michael-Michael-Henry process to diastereoselectively construct chiral cyclohexanes. This unique selectivity and reactivity were explained with the double diastereocontrol phenomenon[3].

As part of our synthetic program, we wished to apply our catalysts in the synthesis of biologically active, natural products, namely, indole alkaloids. Thus, we selected 3,4-substituted indole compounds to transform them via efficient enantioselective organotandem procedures to ergot and secergoline type alkaloids. Our results in the asymmetric synthesis of various indole derivatives will be disclosed in the poster.

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Keywords: *Organocatalysis; Alkaloids; Enantioselectivity;*

P-0999

DEHYDROGENATIVE HECK REACTION OF FURANS AND THIOPHENES WITH STYRENES UNDER MILD CONDITIONS

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The Pd-catalyzed direct cross-couplings of arenes with alkenes through C-H activation, also called intermolecular Dehydrogenative Heck Reactions (DHRs), have drawn much attention in recent years.[1]

Among the arenes used in DHRs, furans and thiophenes have received little attention because the former are acid sensitive and the latter require elevated temperatures, due to their higher aromatic resonance energy and stability. Moreover, styrenes are electron-rich compounds and are a notoriously difficult substrate class due to facile polymerization and cleavage under palladium oxidative conditions.

In 2008, we have reported the synthesis of difurylalkanes through the bis-coupling of 2-alkylfurans with various alkenes, including styrenes.[2] Then, we reported a dehydrogenative coupling of furans and styrenes leading to Heck-type products which allowed the use of chlorinated and fluorinated substrates.[3]

The previous transformation occured under mild conditions but nevertheless, brominated substrates were reluctant to react. Glorius et al. have recently shown that brominated compounds can be formed with no proto-debromination using Rh catalysts; however few examples have been reported and the scope of substrates remains to be developed.[4] We will present the DHRs, under mild conditions, of furans and thiophenes with styrenes, including brominated substrates.[5] The influence and the role of the oxidizing agent on the activity of the catalyst will be also discussed.

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Keywords: *C-H activation; Cross-coupling; Heck reaction; Palladium; Homogeneous catalysis;*

P-1000

FLUORESCENT CORE DENDRIMERS – PHOTOPHYSICAL PROPERTIES STUDY

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Dendrimers are repeatedly branched macromolecules, which have been widely studied because of their intriguing properties as part of light-harvesting or charge-transport systems, catalysts or drug delivery systems.[1]

In this work a set of dendrimers with Fréchet's polyaromatic dendrons[2] and a fluorescent core consisting of natural dye apigenin was prepared. Convergent method of dendrimer synthesis was applied in order to gain sufficient control over final products structure, confirmation of which was provided mainly by NMR spectrometry and MALDI-TOF mass spectroscopy. The four new fluorescent dendrimers obtained, tri-*O*-methyl and tri-*O*-benzyl apigenin were used as subject compounds for photophysical properties comparison, with focus on fluorescence quantum yield and excitation state half-time as well as evolution of their ultraviolet absorption spectra. As the group of prepared compounds is possessing identical fluorescent core, progressive growth of number of aromatic layers in their dendritic branches enabled us to observe the influence of aromatic periphery on the dendrimer center.

Interesting non-linear development of fluorescence quantum yield along with growing dendrimer generation number was observed as well as bathochromic shift in absorption spectra which was previously reported in case of metalloporphyrin cored polyaromatic dendrimers.[3]

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Donostia International Physics Center (DIPC).

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Keywords: *Dendrimers; Fluorescence;*

P-1001

PHOSPHONATE METAL ORGANIC FRAMEWORKS

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Phosphonates metal organic frameworks (MOF) are a very important class of compound with special properties, fascinating network topology and structural flexibility. Cobalt vinylphosphonate was obtained in our labs by the reaction of $Co(NO_3)_2 6H_2O$, vinyl phosphonic acid in equimolecular ratio and hydrothermal conditions. The synthesized compound was characterized by FTIR, elemental analysis, X-Ray crystallography, thermogravimetric analysis and quantochemical calculations. In order to compare the calculated and experimental geometric properties of the cobalt vinylphosphonate metal organic framework we performed a PM3 semi-empirical analysis of structural properties. For this reason five octahedral models were calculated: three arising from constructed geometries and two from experimental RX data[1, 2]. From the PM3 semi-empirical results the calculated bond lengths, bond angles and torsion angles are lower or comparable than the experimental ones. The LUMO-HOMO energetic difference decreases from the simplest to more complex model reaching to a value of 1.465 eV. Belonging to the same group of the periodic table of the elements cobalt and rhodium are expected to have the same electrical behavior. Using the same model, calculations were performed for rhodium vinylphosphonate. As is expected, in the case of rhodium vinylphosphonate, the LUMO-HOMO energetic difference decreases from the simplest to more complex model reaching to a value of 2.168 eV. This small difference allows one electron transition from the superior level into a conduction band and predicts the semiconductor properties of these compounds.

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Keywords: *metal phosphonate; semiempieical calculations; semiconductors;*

P-1002

MEMORY OF CHIRALITY OF TERTIARY AROMATIC AMIDE:APPLICATION TO THE ASYMMETRIC SYNTHESIS OF S ALPHA METHYLDOPA AND NONPROTEINOGENIC AMINO ACIDS

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Compounds possessing 'axial chirality' around a sigma bound are of great interest in asymmetric synthesis, especially in the field of chiral ligands (BINAP). Among these compounds, tertiary aromatic amides (*eg*. Benzamides, anilides), suitably substituted at the aromatic ring or at nitrogen, present 'Dynamic Axial Chirality', and have been less studied. Since 2005, Dr. V. Alezra and Pr. C. Kouklovsky have been developing some asymmetric synthesis of non proteinogenic quaternary/tertiary α-amino acids, based on 'Dynamic Axial Chirality of tertiary aromatic amides' and on the 'Memory of Chirality' (MOC)/ 'Frozen Chirality' (FC) principle.[1–3]

The objective is the application of this methodology for the synthesis of (S)-α-methylDOPA, a well-known quaternary amino acid, used in the treatment of hypertension, proceeding by the concept of 'MOC-alkylation', the only source of chirality being the starting D-alanine. The strategy involves **i**) the conversion of D-analine to its tertiary naphthamide, initial central chirality of the starting amino acid is transferred and induces an axial chirality to 1-naphthoyl oxazolidinone, **ii**) careful deprotonation/alkylation of the oxazolidinone, the axial chirality is retained while the central chirality is lost during enolization, **iii**) optimized deprotection of the oxazolidinone resulted (*S*)-α-methylDOPA with 98% *ee* after five steps.

In continuation of our work, we envisaged the asymmetric synthesis of non proteinogenic β-hydroxy-*α*-amino acids by the above developed methodology and the real challenge is the diastereoselective creation of a second asymmetric center. We are able to extend this from MOC-alkylation to MOC-Aldol reaction.

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Keywords: *Asymmetric synthesis; Amino acids; Aldol reaction; Chirality;*

P-1004

THE FIRST CYCLOPENTADIENYL NICKEL COMPLEXES BEARING A SILYL SUBSTITUTED PHOSPHINE CHELATING SIDECHAIN

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Since the first report on a cyclopentadienyl complex with a transition metal bearing a pendant Lewis base functionalized ligand by Mathey et al. in 1978, this area has developed rapidly. This class of compounds exhibits a great potential in catalytic reactions in terms of catalyst improvement, stabilization of otherwise unstable intermediates and influence on stereochemical and stereoelectronic properties.

In particular, complexes with a tertiary phosphine derivative in a sidechain have attracted much attention. A phosphine group acts as a soft electroneutral σ donor as well as a good π acceptor, capable at the same time of reversible coordination.

The only known secondary phosphine pendant cyclopentadienyl complexes are those of zirconium and hafnium, reported by Ishiyama et al. in 2002. Since these complexes contained a reactive phosphorus-hydrogen bond, they were converted into the corresponding phosphide-substituted cyclopentadienyl chelate complexes. Both systems were successfully applied in catalytic ethylene and styrene polymerization reactions as well as in ethylene/styrene copolymerization reactions.

To our knowledge, no analogous complexes of late transition metals containing a phosphorus-hydrogen or a phosphorus-silyl bond have so far been reported. We now report on the synthesis of the first cyclopentadienyl nickel complexes bearing a silyl substituted phosphine chelating sidechain. We intend in the future to cleave selectively the silyl substituent at phosphorus by treatment with a fluoride reagent, generating thus the first cyclopentadienyl nickel chelating phosphide complexes.

Keywords: *Cyclopentadienyl ligands; Phosphane ligands; Chelates; Nickel;*

P-1005

RECENT ADVANCES TOWARDS THE SYNTHESIS OF RUBROMYCINS

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The rubromycin family is a class of natural products which is known for exhibiting antibiotic, cytostatic and antimicrobial activity. This type of natural products is characterized by a challenging molecular architecture whose basic structure consists of a highly functionalized naphthoquinone moiety which is linked to an isocoumarin unit by a 5,6-spiroketal core.[1, 2]

In continuation of our long standing interest in the synthesis of rubromycin and heliquinomycin we here describe our recent results concerning **a**) the improved synthesis of model substrates, **b**) new insights into the process of the acid promoted ketalization of benzannuated precursors and **c**) the challenges and problems which still have to be solved.[3, 4]

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Keywords: *Natural products;*

P-1006

A CHEMICAL SYNTHESIS OF DANSYLATED UDP-MURNAC-PENTAPEPTIDEFOR HIGH THROUGHPUT MRAY ASSAYS

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Because of the increase in bacterial resistance, the discovery of new antibiotics is of high relevance. The membrane-associated enzyme MraY, which catalyses the transfer of a glycosylphosphate-pentapeptide moiety onto a lipophilic membrane anchor in the course of bacterial peptidoglycan formation, represents an attractive target for the development of new antibacterial agents[1,2]. This enzyme is inhibited by the naturally occurring muraymycin nucleoside lipopeptide antibiotics[3]. The fluorescently labelled MraY substrate is required for high throughput MraY assays as reported by Stachyra *et al.*, who used the dansylated derivative of UDP-Mur*N*Ac-pentapeptide for an *in vitro* MraY assay[4]. A chemical synthesis of dansylated UDP-Mur*N*Ac-pentapeptide is desired in order to obtain an adequate amount, while the isolation from bacteria and subsequent dansylation of UDP-Mur*N*Ac-pentapeptide affords only a small amount of the desired product.

Starting from commercially available *N*-acetylglucosamine, a protected glycosylphosphate precursor was prepared over seven steps in an overall yield of 30%. The peptide unit was synthesised using Cbz-protection of the amino function and different peptide coupling procedures. A novel convergent [4+1]-strategy for pentapeptide assembly gave the dansylated glycosylphosphate--pentapeptide. Following debenzylation and diphosphate coupling with a reactive uridine derivative, the target compound was obtained after final global deprotection. Latest results on this synthetic approach will be presented.

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Keywords: *Antibiotics; Carbohydrates; Fluorescence; Nucleotides; Peptides;*

P-1007

GRAFTING OF POLY(1-SUBSTITUTED VINYLTRIAZOLE) ONTO COLLOIDAL SILICA AND SELECTIVE COORDINATION TO TRANSITION METAL ION

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Triazole compounds exhibit characteristic properties coming from π-conjugated five-membered ring with lone pair electrons for complex formation with transition metal ion. In this work, synthesis of poly(1-substituted-4-vinyl-1,2,3-triazole) and grafting of hydrophilic poly(vinyltriazole) to colloidal silica for application to selective extraction materials of transition metal ion.

We examined two synthetic routes via (**a**) "One Pot" reaction and (**b**) polymerization of vinyltriazole, through "Click reaction". In Route (**a**), poly(1-octyl-4-vinyl-1,2,3-triazole), **1a**, was obtained in 58% yield, but 2-(2-(2--hydroxyethoxy)ethoxy)ethyl-substituted polymer, **2b**, was given in low yield of 4%. Radical polymerization of vinyltriazoles in Rout (**b**) afforded polymer **1a** of molecular weight 24,000 in high yield of 93%, and **2b** and 1-(2-hydroxyethyl)-substituted polymer, **2c**, of molecular weight of 7,000 and 15,000 in relatively high yield, respectively. The reaction of colloidal silica, of 140 nm in diameter, with poly(4-vinyl-1,2,3-triazole)-trimethoxysilane with 2-(2-(2-hydroxyethoxy)ethoxy)ethyl at 1-position gave high disperse polymer-grafted silica in aqueous solution. The hybrid particles selectively captured transition metal ion, Ni^{2+}, Cu^{2+}, Zn^{2+}, stability constants of which were in the range from 1.4×10^3 to 3.6×10^3, being 10^2 times higher than those of alkali earth metal ions, Zn^{2+} and Mg^{2+}.

Keywords: *Poly(vinyl triazole); Colloid; Grafting; Complexation;*

P-1008

INTRAMOLECULAR CYCLIZATION OF 6-HYDROXYALKOXYPURINES

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This work is aimed at the synthesis of tricyclic derivatives of guanine and hypoxanthine. The *O*⁶-Alkylguanines are recognized inhibitors of the *O*⁶-alkylguanin-DNA-alkyltransferase (AGT). Due to this inhibition, the derivatives are cytostatic by increasing the effect of O-alkylations on purine bases in tumor cells caused by alkylation agents. These derivatives are therefore potentially biologically active.

The cyclization reactions were performed with 6-hydroxyalkoxypurines bearing chains of various length, which were prepared by two-step synthesis via corresponding "DABCO-purines" and following alkoxylation with a diol (ethane-1,2-diol, propane-1,3-diol or butane-1,4-diol) in the presence of a base.

The intramolecular cyclization proceeds via the terminal hydroxy-group transformation to a better leaving group. Appel reaction (Ph_3P/CBr_4) was found to be the most fruitful method leading to tricyclic derivatives by group transformation followed by immediate cyclization. The highest yield (64%) was achieved in the case of 2-amino-6-(3-hydroxypropoxy)purine as a starting material. Mitsunobu reaction (Ph_3P/DIAD) was found to give the same products as well. These two methods were applied for the synthesis of derivatives with five- and six-membered rings. Formation of the seven-membered ring has not been achieved.

All the intramolecular cyclizations of 6-hydroxyalkoxypurines proceed on the *N*1 site of the purine moiety as confirmed by two-dimensional NMR.

Keywords: *tricyclic analogues of purines; Appel reaction; Mitsunobu reaction;*

P-1009

THE STUDY OF INFLUENCE OF MICRO ADDITIVES OF SINGLE-WALL CARBON NANOTUBES ON STRESS-STRAIN PROPERTIES AND STRUCTURE OF NOVEL POLYURETHANE BLOCK COPOLYMERS

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Carbon nanotubes are capable to change properties of polymers, such as mechanical strength, the Young modulus, the tensile strain etc. However, the insufficient attention is given to studying of influence of micro additives of single-wall carbon nanotubes (SWCNT) on the polymers structure.

Polyurethane block copolymers (PUBCP) were synthesized for the first time in the present work by interaction of oligodiethylenglycol adipate (ODGA, crystallization temperature $T_c = 60$ °T), of the mixture of diisocyanates and of agents of chains extension in solution at room temperature. The influence of micro additives of SWCNT on stress-strain properties and structure of PUBCP was studied.

PUBCP possess quite high Young modulus (about 450 MPa) up to T_c. It undergo orientation deformations up to 900 % with forming of the strong rigid films (rupture strength ~ 45 MPa) at stretching after achievement of the limit of forced rubberlike elasticity. The oriented samples completely restore their initial sizes at the heating above T_c.

Introduction of SWCNT in PUBCP (0.002–0.008 wt. %) leads to various changes of stress-strain properties and structural parameters. Changes of supramolecular structure of polymer under the influence of SUNT consist in increase in the Young modulus and tensile strain for 20-30 %. Thus, tensile strength of the filled and unfilled samples does not change practically. The SWCNT additives influence noticeably on relaxation behavior of polymer. Thus, recovery of the initial sizes of the samples, containing up to 0.008 wt. % of SWCNT, after deformation requires more high temperatures and prolonged time in comparison with unfilled samples.

Data of DSC and analysis of X-ray diffraction patterns of PUBCP, containing SCNT, testify considerable structural changes in comparison with unfilled polymer. The reasons of influence of SCNT on structure and properties of synthesized PUBCP are discussed.

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Keywords: *Polyurethane block copolymers; single-wall carbon nanotubes; stress-strain properties and structural parameters;*

P-1010

EFFECT OF PYROLYSIS CONDITIONS ON THE SPECIFIC SURFACE AREA OF CARBON AEROGELS

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Carbon aerogels are relatively novel carbon materials with unique properties. An aerogel is mainly mesoporous solid state material containing up to 95 vol. % of air[1]. These materials can be obtained by pyrolysis of organic aerogels, which are prepared by sol-gel polycondensation of certain organic monomers such as resorcinol and formaldehyde[2]. Due to the ability to control their pore texture via the synthesis, drying and pyrolysis operating variables, the properties of these materials can be adjusted to fit the application. Carbon aerogels has application such as supercapacitor, hydrogen electrostorage, adsorption medium or catalyst support[3]. Pyrolysis procedure is an important step in carbon aerogel preparation due to increase of their specific surface area. It was prepared acid and alkaline catalyzed organic aerogels and these were pyrolyzed under different conditions. Pyrolysis temperature (400–1000 °C) and time of this process (0.5–4 h) were studied with relation to their specific surface area. It was found that surface area of resulted fragile acid catalyzed carbon aerogels are depended on carbonization temperature. In this case the largest surface area (~900 $m^2 g^{-1}$) corresponds to temperature 800 °C. Contrary resistant alkaline catalyzed carbon aerogels can maintain a relatively high specific surface area up to ~900 $m^2 g^{-1}$ with no respect to the pyrolysis conditions (except 400 °C). Specific surface area of both types of aerogels is independent on the pyrolysis time in studied range.

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Keywords: *Surface analysis; Sol-gel processes; Pyrolysis; Carbon aerogel;*

P-1011

A NEW APPROACH TO BRASSINOSTEROID SIDE CHAIN SYNTHESIS VIA NITRILE OXIDE CYCLOADDUCTS

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Being versatile tools for new C-C bond formation, nitrile oxides are successfully utilized in 1,3-dipolar cycloadditions with olefins for the synthesis of different types of compounds. The heterocyclic adducts, Δ^2-isoxazolines, as the synthetic precursors of amino- and keto-alcohols are the convenient building blocks for natural products and related compounds.

In continuation of our studies on application of nitrile oxide methodology for the synthesis of natural steroids and their modified analogs, here we present a new approach to brassinosteroid side chain synthesis via nitrile oxide cycloadducts with disubstituted steroidal Δ^{23}-olefins.

Steroidal isoxazolines were synthesized by the reaction of acetonitrile oxide with cis-, trans- and cyclic 22-hydroxy-Δ^{23}-olefins, where Δ^{23} double bond was activated with acceptor ester group. Surprisingly, the same set of products (four isoxazolines) was obtained both for cis- and trans- olefin substrates, and this result was not in the agreement with current opinion on the mechanism of 1,3-dipolar cycloaddition as the concerted synchronous one. It was shown that under diazabicycloundecene action the product set could be converted with a good yield into two isoxazolines with a ratio in favor of a product of the desirable (brassinolide-like) stereochemistry.

The structure of new compounds was confirmed by NMR, MS, elemental, CD and X-ray analysis.

The synthesized steroid isoxazolines could serve as the convenient precursors of natural brassinosteroids and their modified analogs, particularly amino and keto derivatives, and the corresponding synthetic routes will be reported. Taking into account unusual stereochemical course of the studied reactions of 1,3-dipolar cycloaddition, asynchronous mechanism of these will be discussed.

Keywords: *Brassinosteroids; Nitrile oxides; 1,3-Dipolar cycloaddition; Steroids;*

P-1012

CHEMICAL SYNTHESIS OF PROTEIN-DOMAIN-ARRAYS

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It is our goal to establish an elegant way to synthesize a variety of protein domains and small proteins by chemical means, to employ them in arrays for assay analysis. Fragment ligation is the method of choice for this total synthetic task. We use an α-peptide-thioester synthesis with a self-purifying effect, to avoid the time- and product-consuming HPLC-purification. We present an Fmoc-based solid-phase creation of peptide thioesters with self-purification, by the use of *Kenner's Safety Catch* sulfonamide-linker. Self-purification is achieved consecutively by (**a**) N-terminal coupling of a cleavable cyclization linker, subsequent macro cyclization to a resin bound side chain, (**b**) activation of the sulfonamide linkage by alkylation, (**c**) thiolysis generates the side-chain bound thioester and detaches all truncation products, washing releases them, and (**d**) TFA cleavage yields the desired full length thioester in high purity.

We are using this methodology to synthesize different SH3 domains of yeast by Native Chemical Ligation. To establish the method we performed a cysteine scan of the SH3 domain SHO1 and YSC84. Therefore 20-40 amino acid long peptide thioesters were synthesized in parallel with excellent purity.

A consequent extension of the prior described method is the direct application of the generated peptide thioester in a Native Chemical Ligation on a solid support. With a tailored cyclization linker, the self-purified and deprotected thioester can be ligated on the resin with a crude mixture of cysteinyl peptides, since only the full length cysteinyl peptide reacts with the thioester; truncations might be washed off after ligation. The ligation product can whether be released from resin by basic treatment, or can be directly applied for usage in an assay, as a convenient on-bead immobilization.

Keywords: *peptides; Solid-phase synthesis; protein design; Bioorganic chemistry; Total synthesis;*

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A
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Abass H. s994
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Abdel-Wahab B. s982
Abedi Lenji M. s1080
Abeyawarathan V. s950
Abou-Ras D. s1222
Aboutaleb D. s1253
Abouzid K. s721
Abramczyk H. s604
Abrams M. s983
Abramson R. s859
Abreu A. R. s1198, s1337
Abu-Bakr S. s1347
Abuein M. s1122
Abuzeid H. s995
Acar M. s1115
Accetta A. s795
Ackermann L. s1014, s1042, s1082, s696
Adachi J. s1179
Adam M. s1125
Adanitsch F. s854
Addadi L. s832
Adhami F. s1209, s883
Adriaan M. s763
Afewerki S. s1012
Afonso C. s783
Agostinho M. s669
Ahlers J. s1052
Ahmad A. s1109
Ahmed I. s650, s903
Ahn B. S. s1182
Aidarova S. s1062
Aijaz Ahmad A. s1332
Aime C. s1238
Aimi F. s709
Akay M. A. s1131, s1142, s610
Akermark B. s1173, s1174
Akermark T. s1173, s1174
Akhmadullina N. s981, s984
Akimov D. s864
Akmese B. s1109
Akpinar G. E. s1263
Akram S. s608
Aksakal D. s1264
Al Anshori J. s1265
Alajarin M. s1272, s1272
Albericio F. s787
Albler C. s998
Albo Y. s904
Albov D. s991
Albu A. M. s1266, s1282
Alcazar Montero V. s1289
Aldabah A. s1109
Aldas Candan O. s998
Aleksandrova G. s721
Alexandre E. s1161
Alexei L. s1254
Alezra V. s1363
Al-Faifi S. s790
Alghamdi A. s790
Ali D. s1123
Ali M. s982
Aliev R. A. s928
Al-Khalaf A. s1264
Allemann O. s1266
Allendörfer N. s1047
Almaiuf A. s1109
Almeida A. R. s1333, s1337
Almeida D. P. F. s1161
Almeida L. s1178
Alni A. s1302
Al-Omar M. s1265
Alonso Doval D. s999
Al-Oweini R. s992
Alper K. s1012
Alt M. s1360
Alvarez De Cienfuegos L. s740
Alvarez R. s1002, s926
Alvarez-Builla J. s1096
Alves C. M. s791
Alves S. s1159
Aly S. s1067
Alzina C. s793
Alzoubi B. s883
Alzoubi B. M. s686
Amadeu De Sousa N. s1340
Amadeu K. S. s818
Amador C. s658
Amaral J. P. s1221, s609
Amaral J. S. s1159, s793
Amato F. s1110
Amatov T. s1305
Amelia M. s1211
Ammann M. s637
Amodio M. s916
Amouri H. s681
Amr A. E. s1265
Amslinger S. s1267, s897
Anamimoghadam O. s999
Ananev V. s1110, s1209
Ananeva V. s1110
Ananjaroenvong E. s1007
Anderson H. s732
Anderson H. L. s1040
Andersson K. H. O. s1308
Andrei-Selmer L. s896
Andrejic M. s860
Andrikopoulos P. C. s823
Andrioletti B. s662
Andronescu E. s1195
Andronova A. s1121
Aneta V. s1359
Anghel D. F. s1034, s1034, s1268, s1269, s1355
Anic S. s1144
Antonio T. s860
Antony L. A. P. s1265
Anzenbacher Jr. P. s1155
Aoun S. s1000
Apak R. s1161
Aphaiwong A. s1000
Apotheker J. s620
Appiani E. s649
Apryshko G. s991
Aradi K. s1361
Archibald S. s607
Ardizzone S. s849
Arenas-Valganón J. s811, s812

Arends I. W. C. E. s1295
Aresta M. s692, s693
Arico F. s661
Ariga K. s1230
Arik M. s1112
Arikan S. s956, s957
Arlt W. s1193
Armaroli N. s1242, s1360
Armentano A. s1167
Arnold R. s1111
Arrabito G. s712
Arriortua M. s948
Arriortua M. I. s1207, s953
Arroyo M. s985
Arsenijevic J. s600
Arslan N. s1094
Arslanoglu Y. s956, s979
Artal V. s1258
Artel V. s1210
Artetxe B. s1203, s961
Artner C. s1236, s964, s979
Asakawa M. s1238
Asano A. s1048
Ascencao C. s906
Ashfold M. s807
Ashfold M. N. R. s808
Ashoka M. s763
Aslandas A. M. s1111, s1112
Assaf K. I. s869
Assfeld X. s821
Ataee A. s941
Atakol A. s610
Atakol O. s1131, s1142, s1149, s610
Atanackovic N. s645
Attia S. s958
Atwood J. s836
Aubé C. s1001
Aubert E. s1055, s1055
Aubrey A. s593
Auer A. A. s963
Auroux A. s1199
Aurrecoechea J. s1002
Autenrieth B. s1032
Avellini T. s1211, s1211
Aversa M. C. s940
Axthelm J. s861
Ayan S. s1267
Aydin B. M. s1112
Ayme J. F. s953
Ayora C. s642, s642
Azadi E. s1230
Azizoglu M. s1094

B
Baader S. s1268
Babiano R. s1251, s1252
Babic M. s1263
Babiuch K. s1102
Babka O. s643
Bacalum F. s905
Bach T. s714, s769
Bacher M. s896
Bachl J. s1003
Bachmann T. s964
Backaert F. s1002
Backmann N. s1111
Bäckvall J. E. s1097, s1174, s806
Badamshina E. s1105, s1366
Badamshina E. R. s1309
Badilita V. s905
Baek I. H. s1173
Baghban Salehi M. s1080, s1344
Bai S. s1215
Baik W. P. s1231
Baiula M. s720
Bajenaru I. G. s905
Bajerova P. s1124
Bajerová P. s1131
Baker R. J. s924
Bakish I. s1258
Balali S. s870
Balandier J. Y. s798
Balcar H. s976
Bald A. s825, s867
Baldridge K. s1266, s1276, s859, s862, s878
Baleizao C. s1212, s1239, s1345
Balintova J. s1003
Balk S. s1212
Balla C. s677
Ballarin B. s1216, s1220
Ballini R. s655
Balogh D. s1004, s1190
Balogh G. T. s894
Balteanu D. s644
Banach M. s877
Banas P. s872
Bang E. K. s1004
Baptista A. D. M. A. s1337
Bar L. s605
Baran A. s1268, s1269, s1355
Barandika G. s1207
Barath M. s1027
Barattucci A. s940
Barbe J. M. s1016
Barbera J. s628
Barboiu M. s844
Barbosa J. s916
Barbu-Tudoran L. s1196
Barek J. s1117, s1135, s1139, s1140, s1146, s1156, s1158, s597
Barjega S. s1192
Barlam D. s1224
Barnea Z. s664
Baroncini M. s734, s738
Barreiro M. F. s793
Barrocas B. s1255
Barron L. s600
Barros M. T. s1287
Barroso J. M. s871
Barrow R. s1005
Barta J. s933
Bartel C. s684
Barth J. s745
Barth S. s1213, s850
Barthelme A. s1067
Bartkowiak K. s1425
Bartok A. s997
Bartunek P. s1076
Barzagli F. s665
Bar-Ziv R. s1241, s952
Basaran F. s1141
Basko M. s1005

Basov N. s1171
Bassil B. s933, s985, s989, s992, s992, s993
Bastien G. s782
Bastl Z. s1424
Bastos E. s1279, s674, s861
Batail P. s782
Bati G. s1357
Baudoux J. s1269, s1338
Bauer M. s1015
Bauer S. s884
Bauer W. s695
Baumeister U. s1330
Baumgartner R. s652
Bause M. s884
Bay S. s699
Bayardon J. s1015, s1060
Bayraktutan T. s1113, s1113
Bayramoglu M. B. s979
Bazán B. s1207
Bazzicalupi C. s679
Beaugrand S. s1143
Bebiano S. S. s1204
Becker T. s957
Bediha A. s1148
Bednarek M. s1005
Bednarova E. s768
Bednarova L. s724, s886
Bedrac L. s1304
Beekman A. s1005
Beemelmanns C. s1271
Beer P. D. s863
Begel S. s945
Behnam S. s1213
Behnke T. s903
Behr J. B. s1029
Behrends F. s1013
Bélanger D. s1116, s594
Belbakra H. s1360
Belger K. s1270
Belkhiri S. s919
Bella M. s770
Beller G. s688
Beller M. s756
Belogurova N. s1270
Belting V. s1098
Belvisi L. s720
Ben T. s842
Benaliouche F. s966
Bencivenni M. s726
Bendle M. s688
Benfatti F. s1100
Bennati M. s1241
Benning L. s903
Bentz C. s1271
Berberan-Santos M. N. s1239
Berenguer J. R. s1223, s682
Beretta M. s1195, s834
Bergamini G. s738, s938
Berger A. s1316
Berger R. s1271
Berkessel A. s892
Berna J. s1272, s1272
Bernardes G. s796
Bernardi L. s1091
Bernhardt F. s656
Bernhardt G. s884
Berstis L. s862
Bert K. s1273, s762
Bertrand G. s700
Bertrand L. s1021
Bertrand M. P. s771
Berzina M. s942
Berzins A. s852
Bester K. s1114, s648, s693, s905
Bette M. s989
Betz P. s740
Beves J. E. s953
Bevilacqua V. s1166
Beyer B. s1125
Bezuidenhout D. s700, s974
Bhadra S. s1273, s765
Bialek-Pietras M. s1006
Bianchi N. s709
Bichler B. s971
Bickelhaupt F. M. s819
Bidondo M. L. s906
Biely P. s1027
Bildziukevich U. s1006
Bilge Kocak S. s991
Billeter J. s611
Biocic M. s1145
Bird G. s644
Birge R. R. s812
Birjega R. s1189
Birkner A. s1226
Bischin C. s884
Bischop M. s1286
Bisio C. s843
Bistac S. s1007, s1215, s786, s793
Bitter I. s1281
Bitto F. s970
Bivaud S. s798
Biyiklioglu Z. s986, s987, s987, s988
Bjornholm T. s1229, s1237, s1246, s743
Black J. C. s885
Blackstone V. s688
Blagojevic S. s1144, s1160, s1160
Bláha M. s881
Blahova M. s768
Blanc J. s1101
Blanco A. s914
Blanco Jaimes M. C. s1007
Blanco Suarez V. s735
Blanchard P. s773
Blanford C. s740
Blechert S. s1291, s1316
Bleha T. s811
Bleher O. s1129
Bligh S. W. A. s943
Blobner F. s830
Bocarsly A. B. s693
Bocian S. s1115
Boeuf G. s1214
Boey F. s814
Bogdanovic G. s1020
Bohac A. s898
Bohle A. s1330
Bohlender C. s946
Böhm S. s1352
Böhme U. s689, s967
Boiko M. s1114
Boisbrun M. s1330

List of Authors

Bollmann U. E. s648
Bonacchi S. s749
Bonaccorsi P. s940
Bonacic-Koutecky V. s589, s817
Bonakdarzadeh P. s1008
Bongen P. s1274
Bonifazi D. s731, s805
Bonnefille E. s1198
Bonnet S. s698
Bonnot A. s936
Bonvin D. s611
Borcherding H. s612
Borges S. s874
Borghei G. s608
Borisova A. s984
Börner H. G. s749
Bornscheuer U. s703
Boros I. s1314
Borovcova L. s1129
Borovikova L. s721
Borovska J. s778
Borshchev O. s1214
Bortel G. s1235, s1249
Borys N. s1083
Bosshak A. s995
Botoshansky M. s797
Bottesini C. s1168
Bottger E. s1008
Bottka E. B. s1274
Boucheffa Y. s919, s966
Boudesocque S. s651
Bouffier L. s595, s744
Bougdour A. s714
Bougrine A. J. s1331
Bouhadid M. s802
Bouhadja Y. s980
Bouit P. A. s739, s747
Bourahla K. s1091
Bousquet M. s1143
Boutilier J. s613
Boyd T. s697
Boyes S. s1038
Boyron O. s792
Bozkurt E. s1115
Bracco S. s1195, s834
Braese S. s842
Branco L. s665
Branná P. s1275
Bräse S. s1315
Bratu A. s1160
Brauch S. s1275
Bräutigam M. s826, s830, s862
Bredow T. s816
Breeden S. s1182
Bregadze V. s942
Breitzke H. s1198, s1340
Brem B. s1357
Brendler E. s967, s970
Brendler V. s640
Brenner W. s1308
Brett C. M. A. s595
Brezinova A. s1077
Brida D. s699
Brilman W. s1178
Brito R. s1178
Briza T. s1159
Brogly M. s1215, s793
Broncova G. s742
Brown C.E. s1215, s628
Brown K. s828
Broz B. s1009
Brozek J. s1325
Brozek-Pluska B. s604
Bruensing J. s1120
Bruhn C. s694
Brumm S. s955
Brun S. s1199
Bruneel O. s924
Bruns J. s932
Bruns N. s792
Brusová H. s1204
Brust M. s751
Bryant J. J. s784
Brykalova X. O. s830
Buba A. s1285
Büchel G. s911
Bucher G. s999
Buchholz M. s729
Buchmeiser M. s1104, s1235
Buchmeiser M. R. s1032, s1095
Buchta M. s1155
Buchwald S. s801
Bucki A. s1306
Buckle T. s720
Buckley D. M. s829
Budarin V. s1182, s675
Budesinsky M. s1021, s894
Budka J. s1301
Budnikov H. s597
Bugar I. s827
Bugarcic Z. s1276, s1283, s1312
Bujold K. s730
Bulach V. s1075
Bulut A. s1284
Bunkan A. J. s863
Buntkowsky G. s1198, s1340
Bunuel E. s771
Bunz U. s1360
Bunz U. H. F. s784
Buonerba A. s787
Burel F. s1025, s1049, s1099
Burford N. s946
Bürgi T. s753
Buricova L. s1307
Buriol L. s1272
Burke M. s728
Burlini A. s1255
Bury W. s690
Burzuri Linares E. s736
Buschauer A. s884
Busche C. s666, s999
Busetto L. s681
Buszewski B. s1115, s1116, s601, s619, s857
Butenschoen H. s1363
Butterfield A. s1276
Buydens L. s615
Bykowski D. s1072
Bytzek A. K. s684
Byun J. Y. s655

C
Cadigan C. s660
Cadiou C. s607
Cadis A. I. s1196, s1344
Cafagna I. s1166
Cagli E. s1277, s1277
Cai S. s704
Cakir D. s987, s988
Cakir V. s987
Cakmakci E. s1106, s1107
Calderon-Moreno J. s1192
Calderón-Moreno J. M. s1189
Calhorda M. J. s963
Call A. s949
Calle E. s811, s812, s831
Calvete M. J. F. s1337
Cametti M. s1035
Caminade A. M. s1053, s1336
Campana A. G. s771
Campbell T. s885
Campistron I. s1007
Campolo D. s771
Canadell E. s824
Canadi J. s1076
Canal-Vila J. s925
Canbaz C. s1150
Candeias N. s783
Canotilho J. s1198, s1204
Canta M. s701
Cao Q. s845
Capci A. s1079
Capito F. s613
Capolicchio S. s1278
Cappa F. s1009
Capponi M. s1191
Caprioli F. s763
Carbery D. s1010
Cardenas D. J. s740
Cárdenas D. J. s771
Cardoso A. M. S. s791
Cardoso Do Vale M. L. s879
Cardoso S. s1221, s609
Cardova L. s1278, s1350
Carell T. s1082, s887
Carey A. s985
Carlone A. s735
Carlson E. s716
Carmeliet J. s648
Caroen J. s1002
Carofiglio T. s1172
Caron T. s802
Carp O. s1189, s1192
Carreno M. C. s740
Carret S. s1010
Carrey J. s1240
Carrilho R. M. B. s1198, s1333, s1337
Carvalho F. s718
Carvalho M. D. s978
Carvalho S. s863
Casado J. s811, s812, s831
Casado M. A. s694
Casati C. s1241
Casiot C. s644, s924
Casitas A. s701, s975
Cassani M. C. s1216, s1220
Cassir M. s1143
Castriciano M. A. s1216, s1252
Castro R. A. E. s1204
Castro Ruiz C. A. s1116, s594
Cataldo S. s1217, s1255
Cativiela C. s1003
Cavaleiro J. s1288
Cavaleiro J. A. S. s1001, s1057, s1339
Cebolla V. s1362
Ceccato D. s913
Cecchi R. s1343
Cejka J. s865, s976
Celebi N. s908
Ceoldo S. s913
Cerisoli L. s767
Cerkovnik J. s769
Cermak J. s755
Cernak J. s934
Cernoch Z. s1342
Cernochová J. s1275
Ceroni P. s738, s938
Cerovsky V. s724, s886
Cerullo G. s699
Cervellati R. s722
Cervena B. s1117
Cerveny V. s1147, s605
Cesla P. s1119, s1124
Ceslová L. s1119
Cespedes-Camacho I.F. s811, s812, s831
Cetvati Z. s870
Cha G. S. s1127
Cha J. s1335
Cha J. J. s1105
Chai C. L. L. s1090
Chakravarty H. K. s815
Chamas Z. E. A. s1031
Champavier Y. s1021
Chang C. s910
Chang H. s1164
Chang P. Y. s959
Chaniotakis N. s593
Chapleur Y. s1330
Charleux B. s792
Chárová P. s1131
Chas M. s798
Chatel G. s662
Chatterton N. s943
Chaturongakul S. s890
Chaudret B. s1198, s1240
Chaumontet M. s1187
Cheah S. C. s954
Chee C. s608
Chekanova V. s882
Chen F. s1067
Chen G. s943
Chen L. s660
Chen M. s1203
Chen X. s693, s905
Cherevatskaya M. s1031
Chergui M. s827
Cheung S. T. C. s1162
Chevreux S. s607
Chiang L. s1183
Chimowitz E. H. s666
Chin P. s785
Chira N. s1160, s1166
Chirieac A. s1196, s1197, s1197, s1207

Chladkova B. s1156
Chmelik J. s855
Cho M. s1163
Chodounská H. s778, s1301
Choi J. s926
Choi J. C. s1168
Choi J. S. s1183
Choi S. s1165
Choi S. S. s1167
Choi S. Y. s1172, s609
Choppin S. s1348
Choquesillo-Lazarte D. s740
Chorvat Jr. D. s1247
Chou C. s660
Chouzier S. s823
Christian D. s1015
Chronakis N. s1057, s1079, s799
Chrysos M. s782
Chtchigrovsky M. s658
Chua S. S. s1302
Chuayjuljit S. s1248
Chuburu F. s1214, s607
Chung Y. M. s1163
Churakov A. s981, s984
Ciabatti I. s680
Cibulka R. s1356
Cidlina A. s1279
Cielecka-Piontek J. s895
Cieslak A. s690
Cifkova E. s1117
Cifra P. s811
Cihaner S. S. s899
Cik G. s827
Cintas P. s1251, s1252
Ciotonea C. s1196, s1197, s1197
Cipolloni M. s1218, s1327
Ciriaco L. s647, s906, s916
Cirin D. s875, s875
Císarová I. s1298, s1352
Ciscato L. s861
Ciscato L. F. s1279
Civera M. s720
Claeys M. s725
Claridge T. D. W. s807
Clark J. s1182, s675
Clausen I. s689
Clegg J. K. s733
Clerici A. s767
Clough J. s1053
Co D. s828
Coban T. s899
Cocchi M. s617
Cocuzza C. s722
Codola Z. s949
Coelho J. s783
Coelho M. s1161
Cohen H. s904, s952
Cohen S. R. s1224
Cokesa D. s1152
Colak N. s1141
Collini E. s829
Colobert F. s1348
Coman C. s885
Comba P. s889
Comic L. s950
Comotti A. s1195, s834
Company A. s951, s955
Concina I. s1172, s657
Constable E. C. s996
Conway L. s1280
Cooper A. s1206, s820, s844, s848
Cooper C. s884
Cooper D. G. s656
Copur M. s1111, s1112
Coradin T. s1238
Cordova A. s1012
Corminboeuf C. s813
Cornelissen J. s731
Corradini R. s709, s795
Corral Bautista F. s1280
Correia-Da-Silva M. s718
Cortina J. L. s642
Coskun A. s1211
Cossio F. s1362
Cossio F. P. s819
Cossu S. s1055, s1055
Cossy J. s766
Costa T. s653
Costas M. s1222, s701, s949, s951, s955, s975
Cote G. s928
Cotterell M. s808
Coufal P. s1136, s1136
Courtney T. L. s829
Cox G. s955
Cozzi P. G. s1345
Cozzula D. s756
Creaven B. s1244
Credi A. s1211, s1211, s734
Crivillers N. s835
Cronin L. s1217, s1253, s1254, s666, s697, s733, s999
Crucianelli M. s728
Cserep G. B. s1011
Csincsi A. I. s1314
Cuadro A. M. s1096
Cuba V. s928
Cuerva J. M. s740, s771
Cui Y. s594
Cujova S. s886
Cunha-Ribeiro L. M. s718
Curinova P. s1301
Cussó O. s951
Custer L. s1124
Cvacka J. s1130
Czakler M. s964
Czanikova K. s1247
Czirok J. B. s1281

D
Da Ros S. s1281
Dag A. s1067
D'Agosto F. s792
Dahal P. s1039
Dahaoui S. s1075
Dahlmann H. A. s1011
Dalcanale E. s1058, s1242, s797
Dallas L. s638
Dalmadi I. s677
Dambruoso P. s916
Damian G. s674, s884, s888
Daneshgar P. s867
Daniel V. s857
Daniela M. s1342

Dankesreiter S. s1031
Daphne H. s914
Dard M. s705
Daresta B. E. s916
Daru J. s1357
Darwish M. s758
Dasadia A. s850
Date A. s966
Davidova G. s991
Davis B. s796
Davis B. G. s807
Davison W. s650
De Angelis F. s728
De Bank P. s726
De Cicco M. s1067
De Cola L. s839
De Gennaro G. s916
De Kimpe N. s764
De La Escosura Muniz A. s1256
De La Mata F. J. s787
De Lafontaine Y. s648
De Leon F. s931
De Meijere A. s684
De Miguel M. s1212
De Nanteuil F. s1100
De Pablo J. s642
De Pace A. s620
De Simone F. s1100
Deac F. s884, s888
Debouttiere P. J. s1198
Déchamps I. s607
Dei L. s632
Deiana L. s1012
Dejlová B. s896
Dejmkova H. s1117, s1139, s1158
Dejon L. s1353
Del Rosal I. s788
Delachat A. s813
Delaite C. s786, s793
Delalu H. s1176, s1331, s654
Delay M. s909
Delcombel R. s898
Deleanu C. s1336, s1359
Delevoye L. s788
Delgado J. L. s739, s741
Delgado R. s941
Delgado-Martin J. s925
Delile S. s1143
Delley R. s1280
Delogu G. s1013
Delpoux S. s924
Demarinis Loiotile A. s916
Demin S. s608
Demir N. s907, s914
Demirci Cekic S. s1161
Demircivi P. s647
Demir-Ordu O. s1012
Denat F. s1016
Denecke M. A. s639
Deng J. s1319
Denizli G. s1131
Dernedde J. s1246
Desbois N. s1016
Desharnais B. s1067
Deshmukh R. s1217
Desilles N. s1099
Dettori M. A. s1013
Detweiler Z. M. s693
Devadoss A. J. s1118
Devaux E. s746
Deylova D. s1156
Dezileau L. s644
Dezortsev S. s864
Dhar B. s1003
D'Hooghe M. s764
Di Bitonto L. s692
Di Gilio A. s916
Dian J. s742
Dias L. D. s1337
Dias R. D. S. s1333
Diaz Diaz D. s1003, s1046
Diaz-Cuadros J. C. s1282
Dibenedetto A. s691, s692, s693
Dibla A. s1282
Dickschat A. s1013
Diculescu V. C. s598
Didu A. s1118, s1119
Didu M. s1119
Diederich F. s1360
Diers E. s1014
Dietz C. s948, s950
Dietzek B. s699, s704, s781, s826, s830, s862, s864, s893, s988
Dikbas N. s908, s908
Dillenberger S. s1340
Dinisová P. s1119
Dionisio M. s1058
D'Ischia M. s728
Divac V. s1276, s1283, s1312
Djanashvili K. s1295
Djordjevic D. s907
Djurdevic V. s907
Do Vale M. L. C. s791
Dodel R. s896
Doerfler J. s1283
Dogan O. s1264, s1267, s1277, s1277, s1284, s1284
Doistau B. s1259
Dold B. s640, s644
Dolezal M. s1305, s1346
Doll K. s1200, s851
Dolomatov M. s864
Domingo C. s666
Dommer S. s1193
Domokos E. s1188, s917
Donahue L. s1014
Donath M. s946
Dondi F. s631
Dong A. s1215
Dong Z. s814
Donnadieu B. s700
Donnio B. s1282
Doong R. s1183
Doong R. A. s1175, s959
Dorazco A. s932
Dorkó E. s1329
Dorman G. s664
Dörr G. s699
Dorraji P. s890
Dossena A. s1168, s726
Dott W. s1120
Doubnerova V. s1136
Doye S. s1283, s1306

Drasar P. s1066
Drabowicz J. s1046
Dracinsky M. s1077
Dragisic V. s645
Dragoi B. s1196, s1197, s1197, s1207
Dragone V. s1253
Drahos L. s1281
Dralle K. s983
Drasar P. s1035, s1066, s1086, s1089, s1101, s1108, s1278, s1307, s1350, s1354, s1362, s1367
Draye M. s662
Dreiack N. s1358
Dreyer C. s1052
Driess M. s702
Drillaud N. s780
Driver S. s808
Drmanic S. s1065, s1334
Drouza C. s1169, s1169, s673, s673, s686
Drweesh S. s982
Dusek M. s865
Duarte A. s1120, s1221, s1287, s609, s909
Duarte A. C. s651
Duarte B. s718
Duarte K. s1120
Duarte K. R. s909
Dubreuil D. s1001, s1056
Ducho C. s1318, s1364
Duczak N. s1257
Dudenko D. s1330
Dudic M. s1218, s1352
Duchstein P. s826
Dukhopelnikov E. s882
Dukic S. s1214
Dulaiova H. s635
Dumitrescu D. G. s844
Dumitriu E. s1197, s1197, s1207
Dunphy E. s954
Dupont L. s651
Duprez D. s1196, s1197, s1197, s1207
Dupuis F. s1330
Duric S. s1285
Durko G. s1249
Durmaz H. s1067, s998
Durmus M. s969, s986, s988
Duroux J. L. s1021
Dusek M. s1021
Dutartre M. s1015
Dutremez S. s1287
Dvorakova D. s1147
Dvoretskov R. s1134, s1157
Dyballa K. s756
Dzhakipbekova D. s1180
Dzhakipbekova N. s1180
Dzidzigury E. s1232
Dzik W. s1285
Dzik W. I. s1273, s765
Dzubak P. s722

E
Eaton T. s1218
Eavani S. s1250
Ebbesen T. W. s746
Eberhagen F. s1032
Echterhoff A. K. C. s773
Ecker G. s1339
Eckert H. s1013
Efferth T. s1079
Efimenko I. s981
Efimov M. s1219
Eggenspiller A. s1016
Ehrenberg H. s995
Ehterami N. s1016
Eichenauer N. C. s1286
Eichenseer C. M. s1017
Eigner V. s1299, s1301, s1367, s865
Einax J. s911
Eisenhofer A. s1286
Eisner A. s1131
Ekberg C. s928
Ekrem K. s918
El Azzouzi M. s909
El Hajj A. s1331
El Hassan N. s1075
El- Senousy W. s1294
Elahe A. s859
Elbayaa R. s1018, s1018
Elbaz-Poulichet F. s644, s924
El-Beltagy D. s1017
Elbert T. s722, s894
El-Borai M. s1017
Elias M. s1121
Elisabetta B. s1342
Eliseeva M. N. s1281
Elizarov N. s1018
Elke D. s905
El-Rais M. s1121
Elsakhawy M. s1063
El-Seidy A. s982
Elstner M. s1118, s1122, s861
El-Zahany E. s982
Emery D. s800
Emmerling F. s709
Enascuta C. s1177
Enders D. s763
Endoh T. s899
Ene C. D. s1336
Enthaler S. s1302
Eom M. O. s1167
Er E. s1244
Erdogan A. s1094
Ergun E. s1131
Ergun U. s1131
Eriksson K. s806
Erker T. s718
Ermilova M. s1171, s1219, s1248
Ermolatev D. s784
Ermolovich Y. s1107
Ernst S. s699
Ertl G. s588
Erythropel H.C. s656
Esmaeeli M. s918
Esser B. s612
Essid E. s902
Esteves C. V. s941
Estrin Y. s1105, s1366
Etorki A. s1121, s1122
Eul M. s932
Eusebio E. s1198
Eusébio M. E. S. s1204
Eva D. s817
Evren D. s969, s971

Exnerova M. s1338
Eychmüller A. s730

F
Fabbri D. s1013, s659
Fabbri E. s709
Faber K. s705, s802
Fabian I. s688
Fabio P. s1342
Facca C. s913
Faderl C. s1180
Faggi C. s940
Fagnere C. s1021
Fähnemann S. s709
Fahrnbauer F. s851
Fahs A. s1215
Fahsi K. s1287
Faigl F. s1004, s1190, s1274
Faísca Phillips A. M. s1287
Fakhoury J. s730
Fakhre N. s1123
Falcon-Suarez I. s925
Falini G. s659
Falk F. C. s1070
Färber C. s694
Fargasova A. s1219
Farinha J. P. s748
Farinha J. S. s1239
Farinola G. M. s1286
Farkas E. s886
Farsijani S. s1061
Fattah Z. s744
Fazzini P. F. s1240
Fazzini S. s1220
Fedaoui D. s980
Fedotov P. s1149, s603
Feixas F. s871
Fejfar A. s927
Felbermair E. s982
Feldmann K. O. s947
Félix D. s879
Félix V. s863
Femoni C. s680
Feng H. s1103
Feng X. s1271, s1333
Feng Z. s1103
Fenger R. s752
Fenselau C. s728
Fenske D. s1081
Ferenc F. s1313
Ferenczi-Palko R. s1029
Feringa B. s736
Fernandes A. s647
Fernandes C. I. s978
Fernandes I. P. s793
Fernandes R. X. s815
Fernández De Luis R. s953
Fernandez I. s819
Fernández-Calderón M. C. s1251
Ferrara G. s1166
Ferreira J. s1288
Ferreira M. J. s793
Ferrer A. s617
Feulner P. s830
Fey S. s704
Feyzi M. s1213
Fialkowski M. s1260, s746
Fidalgo-Maijuan A. s1207
Figo V. s1217
Filimonov V. s1317
Filip J. s1231
Filipovic M. s944
Filo J. s1019
Fin A. s999
Fingerhut A. s1024
Fink K. s608
Fink M. J. s707
Fisar Z. s1154
Fischer C. s1019
Fischer C. H. s1222
Fischer F. s752
Fischer J. s1119, s597
Fischer R. A. s939
Fisher-Fodor E. s888
Flament S. s1330
Flefel E. M. s1265
Fleischer I. s756
Flesch R. s830
Flidrova K. s1288, s1352
Flitsch S. L. s740
Florea Spiroiu M. s1269
Florencio M. H. s1151
Florjanczyk Z. s1311
Fluxa V. s669
Focant J. F. s906
Foerstendorf H. s640
Fojta M. s1003
Fomin M. s1123
Font M. s975
Forczek S. s1101
Forczek S. T. s1321
Forgione P. s1067
Fornelli L. s602
Forster J. s984
Fort Y. s1031
Foulquier S. s1330
Fraaije M. s708
Frahm R. s1249
Fraix A. s751
Francesco G. G. s1342
Franco-Pujante C. s1272
Francuz J. s1020
Franchi P. s1241
Frank H. s619
Franke A. s1124
Franke R. s756
Frankova J. s895
Fransen P. s787
Franz A. s754
Fränzle S. s628
Fraser S. s734
Fredy J. W. s735
Freitas A. C. s1120, s1221, s909
Frere P. s1061
Frery N. s906
Frey W. s1032
Freydier R. s644, s924
Friess K. s1090
Frimmel F. H. s909
Frisenda R. s736
Frison E. s1172
Fritzsche M. s1330

Fritzsche R. s1221
Froeba M. s841
Fröhlich J. s1300, s1322, s781
Frontasyeva M. s629, s910
Frumar M. s1206
Frumarova B. s1206
Fruth V. s905
Fry E. A. s812
Frys O. s1124
Fu Y. s1222
Fucik V. s724
Fueldner S. s1031
Fuentes De Arriba A. s1289
Fuentes N. s740
Fuerstner A. s762
Fuchs M. s802
Fuhr O. s1081
Fujie M. s1027
Fujimoto Z. s893
Fujita M. s732, s837
Fujita N. s840
Funa A. E. s600
Fuse S. s1327

G
G. D. R. s900
Gabb D. s697
Gabor L. s817
Gabrielli S. s655
Gaefke G. s1078
Gafa V. s1214
Gagne F. s648
Gagnon C. s648
Gahlon H. L. s1011
Gaidzik N. s775
Gal A. s832
Gal N. s1181
Galandakova A. s1307, s895
Galaverna G. s1168, s726
Galina K. s1037
Galletti P. s1178, s1181, s1289, s659, s722, s777
Gallo V. s1166, s679
Galuszka J. s1117
Gambari R. s709
Gamblin D. P. s807
Gan V. s608
Gandelman M. s760
Gandon V. s757
Ganesan A. s1050
Gaponik N. s730
Garcia F. s794
Garcia H. s1212
Garcia M. s820
Garcia Martinez J. s654, s682
Garcia R. s741
Garcia Turiel M. s1289
Garcia-Borras M. s823, s865, s870
Garcia-Bosch I. s1222, s951
Garcia-Martinez J. s1223
Garcia-Ruiz J. M. s740, s810
Garcia-Simon C. s1222
Garrone A. s704
Garwood M. s1228
Gasilova E. s721
Gaskell S. s727
Gasteiger K. s887
Gates P. J. s772
Gatti M. s1168
Gauglitz G. s1129, s1146, s605
Gauvin R. s788
Gavrila I. s1266
Gazit E. s832
Gebauer M. s1305
Geidel C. s789
Geisel K. s1185
Geissler E. s1186
Geist M. s1223
Gelman D. s1062
Gemeinhardt I. s1246
Gemel C. s939
Genet C. s746
Genovese D. s749
Gentilucci L. s720
Georgiades S. s713
Gerasimova E. s1125
Gerhards M. s699
Gerisch A. s1125
Gessner V. s968
Gessner V. H. s695
Geyer A. s711, s896
Geyer J. s902
Gezici O. s750
Ghale G. s887
Ghermani N. E. s1075
Ghiasi H. s995
Ghiasi R. s859, s986, s995
Ghidini A. s795
Giacomini D. s1289, s722, s777
Giammarino G. s880
Gibert O. s642
Gigmes D. s770
Gillet J. M. s1075
Gilmour R. s1091
Gilomen B. s1276
Gindre D. s782
Giniyatullin R. s1334
Ginterova P. s1144
Gioia C. s1091
Giorgetti M. s1220
Giralt E. s717
Girshevitz O. s1224
Gjelsvik R. s636
Gjengedal E. s925
Gjorgjeska B. s1126
Gladow D. s1051
Glaesel H. J. s1052
Glaied O. s786
Glante S. s1202
Gläser S. s946
Gliemann B. s766
Glodjovic V. s950
Glueck S. M. s705
Gniewek A. s696
Gobé V. s803
Gock M. s948
Göckel M. s1290
Goeb S. s798
Gohier F. s1061
Gökagac G. s1181
Gokmese E. s1126
Gökmese F. s1127
Göl C. s986

Golling F. E. s789
Gomes H. s1161
Gomes L. s783
Gómez L. s1222
Gómez R. s787
Gómez-Iglesias P. s985
Gomez-Ruiz S. s667, s667
Goncalves A. s1159
Goncalves L. s674, s861
Gonda Z. s1290
Gondek C. s964
Gonzalez F. s1242
Gonzalez Jimenez M. s812
Gonzalez L. s699, s830
González-Jiménez M. s811
González-Martín M. L. s1251, s1252
Goossen L. s1285
Gooßen L. J. s1268, s765
Gorb S. N. s740
Gordana R. s950
Gordillo G. s751
Gori D. s1363
Gossen L. J. s1273
Gotesman S. s904
Gotlib-Vainshtein K. s1224
Gottfried O. s1337
Göttlich R. s1087, s902
Gottschaldt M. s1102
Goulley J. s723
Gourdon A. s1058, s737
Goux-Henry C. s662
Grabowski M. s1291
Gradert C. s938
Graf C. s1246, s729
Grampp G. s1128, s880
Grancicova O. s827
Grasserbauer M. s653
Grassi A. s787
Gratzer K. s1020
Greb L. s1071
Greenberg M. s713
Greenvald I. s818
Greenway G. s645
Gref R. s751
Grilliez-Vuissoz I. s1330
Grimm B. s739
Grishchuk A. s1105, s1366
Grishina A. s1021
Grmela A. s643
Gröger D. s1246
Gronnow M. s1182, s675
Gros C. s1016
Gross J. s705
Gross Z. s678
Großmann A. s1291
Grötli M. s1049
Grubbs R. H. s592
Gruber B. s1224
Gruber K. s705
Grün C. H. s869
Gruner N. s766
Grupe S. s760
Gu H. W. s1127
Gualandi A. s767
Guclu K. s915
Gueckel K. s640
Guégan J. P. s854
Guenet A. s735
Gueye R. s1021
Guillemin J.C. s854
Guillon D. s1282
Guisado-Barrios G. s700
Gül A. s956, s957
Gülak S. s1022
Gulder T. s1292
Gulder T. A. M. s1292
Guldi D. s1308, s803
Guldi D. M. s739
Guldner L. s906
Guler B. s1022
Gulyakevich O. s1107
Gunay U. S. s1067
Gunden Goger N. s1128
Gunduz H. s1023
Gungor A. s1106, s1107
Günther A. s639
Gust D. s738
Guthmuller J. s699, s830
Gutiérrez-Zorrilla J. M. s1203, s961
Gutmann T. s1198, s1340
Guyon F. s936
Gyollai V. s664
Gyömöre A. s1329
Gyurcsanyi E. R. s1281

H
Ha Thi Hai Y. s1128
Haag R. s1246
Haas T. s802
Hackner B. s1082
Hadad G. M. s904
Hadade N. D. s1336
Haddawi S. s1264
Hadjichristidis N. s786
Hafezi N. s1293
Hagemeier C. s1082
Hager M. D. s1102, s1102, s1293, s791
Haider A. s985
Haider M. s1339
Hajduch J. s764, s1424
Hajduch M. s722
Hájek T. s599
Hajkova Z. s927
Hakimi M. A. s714
Hakimyoun A. H. s986
Halaszova S. s827
Hall E. s608
Hamaoka T. s606
Hamblin G. s730
Hamburger M. s1360
Hamdy N. s1294
Hameau A. s1336
Hametner C. s1300, s1322
Hamilton-Taylor J. s650
Hammad F. s994
Hammerich M. s1294
Hampel S. s1233
Hamuryudan E. s979
Han K. s1165
Han S. s1335
Hanafi Z. s994
Hanefeld U. s1295, s706

Hanekamp J. C. s676
Hanfland M. s1199
Hanganu A. s1160, s1166
Hanni K. D. s735
Hanquet G. s898
Hansen M. R. s1330
Hanslík E. s920
Hanson B. s928
Hanson P. R. s1036
Hansson O. s1174
Hanusek J. s1092
Hanzlova E. s1295
Happ B. s1102
Harada A. s833
Hari D. P. s1084
Harlander C. s1031
Harmatha J. s1035, s1108
Harrar K. s1074
Harris K. s835, s836
Harris N. A. s980
Harris S. J. s808
Hartinger C. G. s684
Hartmann M. s740
Hartmanova L. s1129
Hartwig A. s1246
Harutyunyan S. R. s763
Harzmann G. s736
Hasell T. s820
Hasenknopf B. s1259, s1319, s735
Hashem A. s995
Hashmi A. S. K. s1007, s1098
Hatami S. s612
Hathazi G. D. s888
Hauke S. s1023
Hauptmann J. s1237
Hausen D. s1296
Havel J. s1110
Havel V. s1296
Havlas Z. s1424
Havlicek L. s777
Havlova V. s923
Havran L. s1003
Hawkett J. s733
Hayes C. J. s703
Haynes C. s1228
Heilmann J. s1025
Heinemann F. s943, s945, s951
Heinemann F. W. s695
Heinrich A. s1297
Heinrich A. C. J. s1054, s772
Heinrich B. s1282
Held F. s1024
Hell Z. s1065
Helm M. s1043
Helten H. s688
Hemgesberg M. s699
Hendel T. s730
Hendriksen P. V. s1203
Henke P. s1225
Henne F. D. s965
Henneicke L. s1056
Hennig A. s612
Henrion D. s1330
Henry M. L. M. s628
Henß A. s684
Heo J. s1206
Herchel R. s934, s935
Herchl R. s1024
Hercigonja R. s1199
Hercko I. s627
Herdtweck E. s1030, s1040, s1099
Herges R. s1081, s878
Hering S. s1339, s718
Herisi N. s1137
Herman P. s891
Hermann G. s704
Hermann P. s1155, s944
Hermann W. s1350
Hernandez Melo D. s1225
Hernandez Rubio O. s1289
Herner A. s1297
Herranz M. A. s741
Herrero-Davila L. s675
Herrmann A. s1079, s796
Herrmann A. K. s730
Herrmann J. s1025
Herten D. P. s882
Hesemann P. s841
Hespel L. s1025
Hess P. s1226
Hesse J. s717
Hessel V. s801
Hesseler B. s1026
Hessler F. s855
Heutz N. A. s1226
Heyerdahl P. H. s925
Hey-Hawkins E. s952
Heymann D. s1000
Hietschold M. s1221
Hilbig U. s1129
Hill J. P. s1230
Himl M. s1026, s1365
Himmel D. s1145
Hinrichs W. s687
Hiraoki T. s1027
Hiratsuka M. s818
Hirsch A. s741
Hirsch A. K. H. s1332
Hirsch J. s1027
Hirsenberger H. s1194
Hirtenlehner C. s968
Hirtopeanu A. s1359
Hissler M. s747
Hizal G. s1067, s998
Hizal J. s1161
Hobbs S. s668
Hocek M. s1003, s1039, s1045, s1093, s724
Hochreuther S. s949
Hodek P. s727
Hodgson D. s1280
Hoeppener S. s849
Hoffman M. s1227
Hoffmann A. s612
Hoffmann K. s612, s903
Hoffmann M. s663
Hofmann C. s1298
Hofmann M. s962
Höger S. s1032, s1078, s1083, s1085, s1324, s1328, s1330, s1335, s1348
Hohenleutner A. s1003, s1028, s1083
Höhn C. s695
Hohne M. s703

Hojdova M. s646
Holan M. s1298, s1305
Holcapek M. s1117, s1132
Holden D. s820, s848
Holy P. s1155
Hollaus R. s1299, s998
Hollosi M. s1357
Holthausen M. s694
Holthausen M. H. s960
Holub J. s1299
Holy A. s1077, s604
Holz M. s1028, s1226
Holzer B. s1300, s1322, s781
Holzhauser P. s1133, s1133
Hong H. s1292
Hong J. E. s1227
Hong W. s1078
Hoof S. s1285
Hopf H. s1056
Hoppe A. s989
Hoppe H. s1293
Horka P. s1130
Horkel E. s1300, s1322, s781
Horn A. H. C. s710, s889
Horn C. s1123
Hornicek J. s1307
Hornoiu C. s1188
Horvath D. V. s1029
Horvath E. s643
Horvolgyi Z. s1237
Hosseini M. W. s837
Hostalek Z. s1300
Hottin A. s1029
Houbenov N. s786
Housecroft C. E. s996
Houskova L. s1158
Hovorka R. s1030
Howes K. s1360
Hrabalek A. s1037, s1064
Hranicek J. s1147, s605
Hrdina R. s853
Hrubosova D. s1162
Hruby T. s1130
Hubbell J. s710
Huber S. s1030, s1099
Huber S. M. s1040
Huc I. s1001, s795
Huc V. s770
Hudecek J. s727
Hudecek O. s1301
Hulot C. s1316
Hülya A. s1292
Hunoldt S. s889
Hunt A. s1182
Hurley K. s1228
Hurski A. s1107
Hutchison J. A. s746
Huuskonen J. s1234
Hwang I. s972
Hwang W. S. s1182
Hylse O. s1323
Hynek V. s1090
Hyslop R. M. s628
Hytteballe S. s1030

I
Iammarino M. s1167
Iapalucci M. C. s680
Ibrahim M. s933, s985, s992, s993
Ibrahimova V. s750
Idelson A. s1032
Ignjatovic L. s1152, s866
Iino K. s662
Ikaheimonen T. K. s635
Ikonen S. s1307
Ilharco L. M. s1220
Ilia G. s1326, s1362
Iliopoulos K. s782
Illi S. s977
Illner P. s958
Ilovitsh T. s1258
Inal E. K. s1131, s1142
Inokuma Y. s837
Inoue C. s1302
Inoue S. s702
Inoue T. s1179
Invernizzi C. s1033
Inzenhofer K. s1303
Ioannou C. s1057
Ionita P. s1268
Iovescu A. s1268, s1269, s1355
Iraqi A. s790
Iremonger S. s843
Irena S. s929
Irsai I. s1303
Isci M. s1277
Ishi-I T. s1033
Isik M. s774
Iskakova S. s927
Iskra J. s1304, s1304
Islam M. M. s816
Isobe H. s1074
Ito Y. s1228
Iturrospe A. s1203, s961
Ivanova A. s1125
Ivanovic-Burmazovic I. s687, s944
Iwaura R. s1229
Izarova N. s697, s989
Izarova N. V. s942
Izzet G. s1239, s681

J
Jäckel E. s639
Jackstell R. s756
Jacobi Von Wangelin A. s1022, s760
Jadhav D. s1041
Jaeger C. s612
Jagerszki G. s1281
Jagtap P. s1305
Jagusiak A. s897
Jahn U. s1298, s1305
Jähnigen S. s967
Jain T. s1229, s1246
Jakab E. s1249
Jakabovic J. s1019
Jakupec M. A. s684
Jalali F. s890
Jalink K. s785
Jalsovszky I. s1249

Jamali S. s941
Jamróz M. s868
Janata J. s593, s638
Jancarik A. s1121
Jandera P. s1151, s1153, s599
Jandourek O. s1305
Jane E. s827
Jang S. J. s1168
Jang Y. M. s1167
Jani A. s850
Jänis J. s869
Jankovic N. s1276
Jansa P. s1077, s604
Jansen M. s1200, s851
Janssens P. s1273
Jarmuz M. s1425
Jaskowska J. s1306
Jaspers D. s1306
Jean L. s1068
Jecmen T. s727
Jedlickova V. s1132
Jelfs K. s1206, s848
Jelinek I. s742
Jelinek R. s1181
Jenkins S. s808
Jennerjahn R. s756
Jenny T. A. s1326
Jensen A. A. s646
Jeon S. I. s1177
Jeong S. s1176
Jeong S. K. s1173
Jerabek P. s866
Jerca F. A. s1034, s1034
Jerca V. V. s1034, s1034
Jessen H. J. s1069
Jester S. s1083
Jester S. S. s1032, s1085, s1324, s1328, s1335, s1348, s745
Jho J. Y. s1052
Ji Q. s1230
Jiang S. s1096, s844
Jiarpinitnun C. s890
Jilek R. s1170
Jiménez T. s771
Jimenez-Diaz R. s1213
Jin M. s1164
Jin S. s937, s972
Jindrich J. s742, s768
Jinkarn T. s1072
Jiracek J. s894
Jirak R. s1154
Jirasko R. s1132
Jochen T. s905
Jofuku K. s1202
Johansson E. M. V. s1307
Johansson M. J. s1308
John J. s928
Johnsen L. s616
Johnson D. B. s641
Johnson M. s654
Johnson T. s758
Johnston E. s1012, s1097, s1173, s1174, s806
Jolanda P. s916
Jolley K. s758
Jonas D. M. s829
Jones A. s645
Jones M. s975
Jones P. G. s1056
Jones R. s664
Jonke A. s593
Jorda R. s777
Jordanovic J. s848
Jorge T. F. s1151
Jorgensen K. A. s801
Josephson L. s720
Joshaghani M. s1213, s1230, s1250, s1250, s941
Josowicz M. s593
Joubert L. s1068
Journot G. s767
Jovanovic B. s1065, s1334
Jozsa E. s649
Judy L. s608
Juge S. s1015, s1060
Juhasz I. s1281
Julien C. s995
Jumean F. s1132
Juncosa-Rivera R. s925
Jung E. M. s893
Jung G. s882
Jung J. S. s1231
Jung O. S. s961
Jung Y. s1176
Jurado A. S. s791
Juraj G. s1359
Juranová E. s920
Jurasek M. s1035, s1086, s1108
Jurcek O. s1035, s1307
Jurcik V. s779
Jurecka P. s868, s876
Jürgenliemk G. s1025
Juris R. s749
Jurkschat K. s948, s950
Justino C. s1120, s1221, s609, s909
Justyniak I. s690
Jux N. s1308, s1322

K
Kachkovskyi G. s1180
Kacirova M. s891
Kafafy A. H. s721
Kafka F. s1305
Kafka S. s1340
Kahler A. s710
Kahnt A. s725
Kainz Q. M. s1017, s1036
Kaiser A. s775, s891
Kaiser M. s968
Kalagaev I. s818
Kalenius E. s869
Kaleta J. s1327, s1424
Kaletova E. s1424
Kalfon-Cohen E. s1224
Kalina J. s1139
Kaliner M. s1036
Kalkan Burat A. s969, s971
Kalkan E. s908, s908, s914
Kalmykov S. N. s928
Kaltbeitzel A. s800
Kamenik J. s635
Kaminska A. s1260
Kaminsky J. s1354
Kamnev A. A. s652

Kamradek M. s1133, s1133
Kandioller W. s684
Kandoth N. s751
Kang S. K. s1037
Kang Y. s1103, s1164
Kani I. s987
Kann N. s1308
Kantekin H. s986, s987, s987, s988
Kaplánek R. s896
Kaplanova M. s1338
Kapras V. s1301
Karabanovich G. s1064
Karabulut M. s1244
Karachevtsev F. s1134, s1157
Karakose A. s1140
Karban O. s1244
Kardos G. s1097
Kardos N. s662
Karel L. s1129
Kargin Y. s984
Karim S. s1173
Kärkäs M. s1173, s1174, s806
Karlikova M. s1231
Karlsson E. s1174
Karnahl M. s988
Karpacheva G. s1038, s1219, s1232
Karpov S. V. s1309
Karsili T. N. V. s808
Kasak P. s1247
Kasarci A. s1126
Kashiwada A. s1232
Kasicka V. s1121, s604
Kassab R. s1104
Kasyutich O. s731
Kataev E. s1111
Katerina C. s929
Kathayat R. S. s1349
Katz T. s689
Kaufmann A. s1233
Kaufmann L. s1233, s1234
Kaurinovic B. s901
Kautek W. s828
Kavelenova S. s901
Kawasaki S. s1365
Kaynar G. s1244
Kebert M. s911
Kebir N. s1049
Keceli G. s920, s921, s921
Keglevich G. s1008
Kehr S. s839
Keinan E. s797
Kele P. s1011, s1297
Keller I. s695
Keller M. s1053, s1336
Kelsen V. s1240
Kempe R. s1303
Kempf N. s977
Keppler B. K. s684
Keramidas A. s673, s686
Kern M. s1038
Kern S. s690
Kervennic Y. s1229
Kesarkar S. s764
Kessler S. N. s755
Kettling U. s657
Kevresan S. s875
Khaleel N. D. H. s904
Khan B. s1285
Khan F. s678
Khipach V. s1107
Khodayari M. s1250
Khom S. s718
Khriachtchev L. s845
Khripach V. s1367, s856
Khusniyarov M. s698, s951
Khusniyarov M. M. s974
Kicková A. s798
Kielkowski P. s1039
Kijenski J. s868
Kilic M. s1193
Kilianova M. s1234
Kim D. s972
Kim D. H. s655
Kim E. s1164
Kim H. J. s1177
Kim J. s1163, s1164, s1184
Kim J. G. s1177
Kim K. s752
Kim M. s1184
Kim S. s1052, s1184, s1184
Kim S. H. s1165, s1168, s1310, s655
Kim S. K. s1134
Kim Y. s937, s972
Kim Y. C. s1039
Kim Y. J. s1177, s1185
Kimoto H. s1048
Kimura Y. s1205
Kinart Z. s825, s867
King D. s808
King R. B. s990
Kingsley J. s790
Kirchner K. s971
Kirsch M. s606
Kirtman B. s870
Kiseleva S. s1038
Kishimoto M. s659
Kiskinova M. s825
Kisko G. s677
Kiss A. s1065
Kiss N. Z. s1008
Kiss V. s649
Kitschke P. s963
Kitson P. J. s1253
Kivala M. s766
Klaas R. s1235
Klán P. s1265
Klapper M. s789, s800
Klasek A. s1342
Klasnja B. s911
Klebe G. s1332
Klementová M. s1305, s1346
Klika K. s1358
Klimes J. s814
Klimesova V. s1037, s1064
Kling M. s729
Klivar J. s1121
Kljun J. s684
Klose F. s805
Klüfers P. s977, s978, s983
Knappke C. E. I. s1040
Knauber T. s1285
Knibbe R. s1203

Kniep F. s1030, s1040, s1099
Knob R. s1144
Knochel P. s754
Knorn M. s1309
Knorr M. s936
Knowles M. s885
Ko Y. S. s1227, s1310, s609
Kober T. s928
Kober V. s940
Koberova M. s727
Koca J. s822, s872
Kocman M. s868, s876
Koch S. s887
Kochel A. s994
Kocik M. s1425
Kocsis G. s725
Kocsis L. s664
Koehler T. s1222
Koenig B. s1031, s1047, s1243, s884
Koenig M. s1102
Koenigs R. s1310
Koetteritzsch J. s791
Kogiso M. s1238
Kohl B. s1311
Köhl I. s1041
Kohler F. s810, s878
Kohler L. s684
Kohls P. s1041
Kohutova A. s1424
Koivula T. s928
Kojic V. s1020
Kojio K. s1365
Koktan J. s1135, s1159
Kolaczkowski M. s1306
Kolar M. s1234
Kolar-Anic L. s1144
Kolehmainen E. s1035, s1066, s1307, s833
Kollár L. s1333
Kolmar H. s613
Kolorosova A. s1147
Kolusheva S. s1181
Komon T. s1311, s868
Komratova V. s1105, s1366
Kondinski A. s989
Kondratuk D. V. s1040
Konecny M. s742
Konieczny L. s897
König B. s1003, s1003, s1025, s1028, s1049, s1083, s1084, s1123, s1157, s1224, s1286, s1318
König N. F. s1234
Kontominas M. s673
Koos M. s1027
Korkuna O. s1114
Kornhaaß C. s1042
Korobova O. s1171
Korotvicka A. s1312
Korshin E. s1042
Kortz U. s697, s942, s985, s989, s992, s992, s993
Kortz U. s933
Korzekwa J. s939
Köse D. A. s1127
Kosinová P. s876
Kosma P. s1299, s854
Kosmrlj J. s1340
Köster H. s1332
Kosterina N. s902
Kostiainen M. s731
Kostic M. s1276, s1283, s1312
Kosugi N. s830
Kotaskova M. s1043
Kotek J. s933, s944
Kothe E. s893
Kotkova Z. s944
Kotora M. s1076, s1088, s1312, s855
Kötschau A. s911
Kouklovsky C. s1363
Kounaves S. s593
Kousalova J. s1043
Kovacic S. s846
Kovacikova L. s898
Kovacova S. s1313
Kovacs E. s1004, s1190, s1313
Kovács H. s912
Kovacs J. s1188
Kovacs S. s1314
Kovacs Z. s1188, s643, s917
Kovaricek P. s1044
Kovats E. s1235, s1249
Kowalski P. s1306
Kowalsky W. s699
Koyanagi S. s1174
Kozaris I. s624, s624
Kozhinov A. s602
Kozien M. s1244
Kozisek J. s857
Kozmon S. s822, s872
Kral V. s1135, s1159
Král V. s896
Kralik A. s1314
Králová J. s896
Kralova K. s1305, s1346
Kramer C. s1315
Kratochvíl B. s1204, s1367
Kratochvil J. s1315
Kraus T. s1021
Kraus W. s709
Krause K. s893
Krause N. s1052, s1098, s1270
Kraushaar K. s689
Krausova B. s778
Krausse N. s1316
Kravets I. s1125
Krchnak V. s772
Krebs M. s1044
Krecmerova M. s604
Krejcík L. s1204
Krejcova Z. s1135
Krenk O. s1315
Kretschmer F. s1293
Kreutzer J. s1236
Kreuzer A. s1045
Krivosudsky L. s956
Krizek T. s1136, s1136
Krizova I. s1021
Kroke E. s689, s964, s965, s967, s970, s973
Krol M. s897
Kronstein M. s1200
Krossing I. s1145
Kroutil W. s802
Krueger A. s740

Krueger M. s1222
Krüger M. s892
Krupa I. s1247
Krupkova A. s755
Krystof V. s777
Kubala M. s1158
Kuballa T. s617
Kubat P. s1225
Kubat V. s1236
Kubatkin S. s1229
Kubeil M. s715
Kubelka T. s1045
Kubicki M. M. s936
Kubickova A. s1136
Kubisa P. s1005
Kuchar J. s934
Kudová E. s778, s1301
Kudryasheva N. s1270
Kudzin M. s1046
Kudzin Z. s1046
Kuehbeck D. s1046
Kuemmel S. s1031, s1047
Kugimiya A. s606
Kuhajda K. s875
Kühl O. s687
Kuhn A. s595, s744
Kuhn C. s1316
Kühn L. s730
Kuhnert N. s869
Kuil J. s720, s785
Kuk J. H. s1163
Kukacka Z. s892
Kukoc-Modun L. s1145
Kukueva V. s809
Kulchat S. s1047
Kuleshova L. s882
Kulhanek J. s1043
Kulkarni A. s851
Kumar K. s804
Kumar S. s1309
Kumbaraci V. s1022, s1023
Kümmerer K. s650, s904
Kumsapaya C. s595
Kun D. s1237
Kunduraci M. s610
Kunes J. s1315
Kunhao L. s654
Kunhardt D. s1233
Kunz H. s775
Kunz O. s1048
Kuo M. Y. s1201
Kupfer S. s699, s830
Kuramitsu R. s1164
Kuramochi H. s636
Kurdi R. s643
Kurka P. s1139
Kurotsu T. s1048
Kursun G. s1127
Kurth D. G. s1223
Kurtz Jr D. M. s888
Kurz P. s1185
Kutonova K. s1317
Kuzmanovic N. s1049
Kvitek L. s1219, s1231, s1234, s1257
Kwak M. s796
Kwon A. H. s1172
Kwon K. s1164
Kwon Y. U. s1172, s1227, s609

L
La Mantia F. s594
La Venia A. s772
Lachaize S. s1240
Lachenmeier D. s617
Lachmann B. s1077
Lacôte E. s1319
Lafarge J. s1049
Lagana A. s623, s623
Lahtinen M. s1307, s1324
Lai J. s1124
Laine T. s1173
Lainer G. s1059
Lair V. s1143
Lajeunesse A. s648
Lako J. s643
Lalinde E. s1223, s682
Lam C. M. s1317
Lambert C. s898
Lan Y. s933
Lanari D. s663
Landgraf S. s1128
Landman M. s945
Lang H. s1221
Lang K. s1351
Lang T. s1318
Lange A. s955
Lange N. s723
Langer J. J. s1425
Langer K. s1425
Lanigan R. s1050
Lara-Avila S. s1229
Larnaud F. s1050
Larranaga A. s948
Lartaud I. s1330
Laschat S. s1044, s1071
Laskay U. s602
Laskova J. s942
Laszlo K. s1186
Latos Grazynski L. s1072
Latronico M. s1166, s679
Laub H. s1051
Laura D. L. C. s1337
Laurin M. s810
Laursen B. s1237
Lazar A. I. s869
Lazar D. s1194
Le Blanc A. s1129
Le Bras J. s1051, s1361
Leask R. L. s656
Lebreton J. s1000, s1056
Lecamp L. s1025
Lechner R. s1047
Lee B. L. s1173, s1174
Lee C. S. s1052
Lee C. Y. s1163
Lee F. W. s1162
Lee G. J. s1134
Lee H. s1164, s1164, s1182, s1183
Lee J. s1127
Lee J. S. s1310
Lee K. s1163
Lee K. I. s1183

Lee L. s1184
Lee M. s1165, s593
Lee S. D. s1183
Lee T. C. s869
Lee W. R. s926
Lefebvre Q. s733
Léger D. s1021
Legrand Y. M. s844
Lehn J. M. s1044, s1047, s1081, s1096, s1293, s588
Lehto J. s928
Lehtonen A. s962
Leibold M. s694
Leigh D. A. s735, s953
Leiner J. s821
Leitner S. s968
Leliege A. s773
Lemercier G. s1214, s607
Lemke A. s1318
Lemouchi C. s782
Lempke L. s1052
Lemr K. s1143, s1151
Len C. s780
Lengyel L. s664
Lente G. s688
Lentsch C. s1009
Leo Y. S. s608
Leonard E. s780
Léonel E. s1001
Leonhardt C. s955
Leonhardt S. s962
Lepoittevin B. s770
Lequeux T. s1050
Lere-Porte J. P. s802
Leridon H. s906
Lesage De La Haye J. s1319
Lesma G. s1343
Lesnichaya V. s1105, s1366
Lesnikowski Z. J. s1006
Lesnyak V. s730
Lestari W. W. s952
Letona R. s931
Levin Y. s1042
Lewandowski B. s735
Lewinski J. s690
Lewis M. s848
Lhotak P. s1288, s1301, s1352, s1354
Lhoták P. s1299, s1351
Li A. s1319
Li M. s1320
Li T. s1237, s1246
Li Vigni M. s617
Li X. s1124
Li Y. s783
Li Z. s610, s839
Lian R. s925
Liao H. R. s1175
Libuda J. s810
Licbinska M. s643
Lichtenecker R. s1009
Lidzey D. G. s790
Lieberzeit P. s929
Liles D. s1208, s974
Liles D. C. s972
Lim H. S. s1165, s1168
Lim J. A. s1173
Lima A. s1175
Lima L. M. P. s941
Limtrakul J. s595
Lin F. s660
Lin Y. S. s1228
Linares N. s682
Linck N. s660
Linclau B. s1050
Lindhorst T. K. s740
Lindner B. D. s784
Lindner L. s978
Lindner W. s602
Ling K. s1053
Ling Y. s1103
Linhardt R. s1053
Linhart I. s1026, s1314, s1365
Linshoeft J. s1054, s772
Lintnerova L. s898
Lippach A. s1320, s1321
Lippold M. s964
Lipshutz B. s856
Lisa M. s1117
Lischka H. s781
Lischke U. s887
Liskamp R. s776
Listorti A. s1360
Liszewska M. s1260
Litus E. s902
Litvinovskaya R. s1367
Liu C. s1206
Liu S. s1083
Liu T. s808
Liu Y. s910
Lloret-Fillol J. s949
Lo Magro S. s1167
Lobanova I. s942
Lodi A. s653
Lodygina V. P. s1309
Loeb S. J. s729
Loget G. s595, s744
Loh T. P. s1302
Löhr A. s628
Lommel T. s891
Long D. s697, s999
Long D. L. s666
Longoni G. s680
Lönnecke P. s952
Lopes A. s647, s916
Lopes C. B. s651
Lopes I. C. s598
Lopes L. M. F. s1220
Lopes M. E. s1137
Lopez Barreiro D. s1178
Lopéz P. s914
López-Aranguren Oliver P. s666
Lopez-Carrillo V. s1345
Lopez-Sanchez B. s1074
Loredo J. s926
Lorente R. s787
Loshchinina E. A. s652
Losse S. s944
Lotfi S. s1054, s1137
Lotz S. s682, s972, s980
Louis S. s648
Loukotova S. s1321
Loullis A. s1165

Löw N. L. s1234
Lu M. s1179
Lu Z. s1319
Lubal P. s1155, s944
Luben G. s1178
Lucarini M. s1241
Ludwig G. s989
Luetzen A. s1329
Luis Carlos S. s1178
Luis J. M. s820, s823, s865, s870
Lumpi D. s1300, s1322, s781
Lundberg K. s1308
Lundell J. s845
Lungerich D. s1322
Lüning Ulrich P. Of. Dr. s1041
Lüning U. s1026, s1068, s1078
Lupan A. s990
Lupan I. s888
Lupenko D. s1323
Luponosov Y. s1214, s1323
Lupton J. s1083
Lützen A. s1030
Lützenkirchen-Hecht D. s1249
Luxenhofer R. s1291
Lux-Steiner M. Ch. s1222
Luz P. s647
Lycka A. s1342
Lydon C. s666

M
Maah M. Hd. Jamil s954
Maalem M. s1138, s1253
Maccato C. s1220
Macícková-Cahová H. s1039
Maciejowska I. s633, s634
Macquarrie D. s1182, s675
Madich Y. s1002
Madybekova G. s1062, s929
Maenhaut W. s725
Maes B. s716
Maggini L. s731
Maggini M. s1172
Mahboobi S. s1089
Mahmood A. s1210
Mahmoodi F. s1250
Mahmoud W. M. M. s650, s904
Mahramanlioglu M. s915, s915
Mai T. T. s1363
Maia E. s626, s931
Maier L. s1323
Maier N. M. s602
Maier S. s1324, s851
Maier V. s1144
Maik S. s990
Maillou T. s1143
Maimon E. s958
Maitani Y. s1238
Maitra U. s1003
Maiuri M. s699
Majdik C. s1303
Majer Z. s1357
Majidi M. s1137
Majlesi K. s870
Majoral J. P. s1053, s1336
Mäkelä T. s1324
Maksimovic J. s1144
Maksimovic Z. s600
Mal S. S. s992
Malferrari D. s1181
Malgorzata S. s1116
Malicka J. s1242
Malig J. s1308
Malinova L. s1325
Malisova K. s1138
Malkov A. s1248
Malkov G. V. s1309
Malter M. s1325
Maltzev E. s1323
Malygin A. s1248
Malz R. s1246
Mamane V. s1031, s1055, s1055
Mammen L. s789
Man I. s1359
Man P. s855, s892
Mandery H. s660
Mani F. s665
Manicardi A. s709, s795
Manke A. M. s1185
Manners I. s688, s954
Manos M. s1057
Manoylova O. s805
Manso J. A. s831
Mantsala P. s1358
Manzoor Ahmad Malik M. s1332
Maougal E. s1056
Maqsood Ahmad Malik M. s1332
Mara L. s905
Maranescu B. s1326, s1362
Maranescu V. s1326
Marchal Ingrain A. s626
Marchelli R. s1168, s709, s795
Marchese L. s843
Marchetti F. s681
Marchi E. s738
Maresová D. s920
Mareda J. s800
Marek I. s1059
Maria T. M. R. s1198
Maric M. s656
Marini F. s614
Marin-Rodriguez C. s1272
Markopoulos G. s1056
Markoulides M. s1057, s799
Markovic J. s600
Maron L. s788
Marques E. F. s879
Marques F. s718
Marrocchi A. s663
Marsura A. s1075
Martharu A. s1182
Marti Rujas J. s836
Martin Caba S. s1326
Martín N. s739, s741
Martinek V. s866
Martinelli C. s1286
Martinez-Espin J. S. s1272
Martini C. s1238, s770
Martin-Lasanta A. s740
Martins F. s874
Martins G. s1255
Martins J. S. s1240
Martins M. A. P. s1272

List of Authors

Martins S. s1239
Martinu T. s1295
Marques E. F. s791
Marvaud V. s735
Maryutina T. s1149
Marzocca A. s916
Masat M. s1327
Mascarenas J. L. s711
Masek V. s1219
Masiol M. s912, s913, s913
Masseroni D. s1058
Mastalerz M. s1311, s799, s847
Mas-Torrent M. s835
Mastrorilli P. s1166, s679
Masui H. s1327
Mata R. s860, s871, s874, s879
Matache M. s1336
Mateos Gil J. s741
Matern A. s1125
Mateus P. s941
Mathé-Allainmat M. s1000, s1056
Matile S. s1004, s1347, s800, s804, s999
Matito E. s820, s871, s876
Matousova E. s1315
Matsko N. s846
Matsuda K. s1232
Matsumoto S. s1179
Matsuno T. s1074
Matt B. s1239, s681
Matthäus C. s893
Matthias S. s958
Mattioli C. s1058
Mattoussi H. s748
Matuska R. s872
Matveeva G. s721
Maubon D. s714
Maulide N. s759
Maurer C. s993
Maxim M. s1269, s1355
May R. s1328
Mayer I. s876
Mayes W. s645
Mayor M. s1218, s1226, s1259, s736
Mayr H. s1051, s1280
Mazal C. s1328
Mazzoni R. s681
McBurney R. T. s953
McElhoney K. s593
McGinley J. s1243
McInnes E. s733
McLaughlin C. s730
McLeod M. s1337
McNeill K. s649, s652
Mechau N. s1360
Mecinovic J. s898
Meda P. s723
Meffre A. s1240
Meguellati K. s1047
Mehdaoui B. s1240
Mehdi H. s1329
Mehlich J. s630
Mehring M. s1221, s955, s962, s963, s990
Meier B. s1059
Meier W. s792
Meireles A. M. C. s1204
Mejuch T. s1059
Melavuori M. s845
Melcher B. s810
Melero J. S. s985
Melo Jorge M. E. s1240, s1255
Memarian N. s657
Mena I. s694
Menand M. s1239
Mende F. s1367
Mendes Da Silva J. F. s761
Menezes R. C. s864, s893
Menna E. s1255
Mennucci B. s815
Ménová P. s724
Mereiter K. s971
Merkoci A. s1256
Merna J. s1300
Meroni D. s849
Merten D. s911
Mertens F. s1202
Mertlikova-Kaiserova H. s1077
Merz K. s1226
Messadi A. s651
Mestek O. s1138
Mestrinho E. s1137
Meszaros A. s1349, s1357
Metrangolo P. s836
Metsa-Ketela M. s1358
Metson J. s975
Meunier Prest R. s1060
Meyer A. s1330
Meyer K. s810
Meyer M. s1330
Meyer R. s639
Meyer S. s1201
Meyer-Eppler G. s1329
Meyer-Ilse J. s864
Meyers S. s633
Meyerstein D. s1241, s952, s958
Mezei P. D. s1281
Meziere C. s782
Mezzina E. s1241
Micali N. s1216
Michaelides A. s814
Michalak A. s1425
Michel C. s823
Michl J. s764, s1218, s1327, s1424
s1424
Micksch M. s960
Micolova P. s722
Mietton F. s714
Mihailescu C. s1268
Mihalache M. L. s1160, s1166
Mihovilovic M. D. s1339, s707, s718, s719
Mika J. s1139
Mika L. T. s1097
Mikes M. s1117
Mikhailovsky S. s1248
Mikhaylov A. s1334
Mikkelsen L. s1203
Mikyskova H. s604
Milan P. s1359
Milata V. s1092, s627, s770
Mildner F. s1331
Milek M. s698, s974
Milek T. s826
Milenkovic M. s866

Milenkovic N. s1188
Milfelner M. s1263
Milione S. s687
Miller B. s633
Millini R. s848
Milstein D. s591
Minca I. s905
Mineo P. s1060
Minko E. s1090
Minois P. s1060
Miras H. s666, s733
Mirmohseni A. s1054
Miro Sabate C. s1176, s1331, s654
Mironova E. s1219, s991
Misicák R. s798
Miskovicova M. s1154
Misztal K. s1242
Mitarai M. s659
Mitchell S. s697
Mitchell T. s625
Mitric R. s817
Miyasaka K. s840
Miyata M. s838
Miyazawa M. s893
Miyoshi D. s899
Mizera J. s1125
Mladkova J. s894
Mlynsky V. s872
Mochizuki C. s1205
Modau E. s1208
Moeller M. s1120
Moffitt M. s748
Mogilireddy V. s607
Mohamadou A. s651
Mohamed S. s1063
Mohammad L. s1054
Mohmmad Younus Wani M. s1332
Mohsen M. s721
Mohtat B. s1061
Moita M. L. s874
Mojmir N. s929
Moldoveanu I. s598
Molina Sanchez P. s1217, s666
Molinari M. s1214
Molon M. s939
Moloney M. s1000
Moloney M. G. s1090
Momma M. s893
Monajjemi M. s867
Monard G. s1330
Monari A. s821
Mondal M. s1332
Mondal S. s771
Mondes V. s729
Monincova L. s724, s886
Monkowius U. s968
Monsu Scolaro L. s1216, s1252, s940
Montalti M. s749
Monteiro O. C. s1255
Montellano P. s1242
Montmeat P. s802
Mooney V. L. s812
Moore A. L. s738
Moore T. A. s738
Morain B. s810
Morales R. s931
Moran J. s1243, s1244
Morandi G. s1025
Moreau J. s1214
Morel E. s735
Moreno M. S. M. s1333
Morgan M. s889
Moriga T. s1202, s1208
Morrison C. s1124
Morscheidt W. s928
Moser F. s631
Mosinger J. s1225, s751
Mot A. C. s674, s885, s888
Mota A. J. s740
Motakef Ghomi M. R. s1209
Moth-Poulsen K. s1229
Motokuchou S. s1365
Motz G. s1303
Mousavi Moghadam A. s1080, s1344
Moussa D. s1104
Moussa J. s681
Moussallem C. s1061
Mracec M. s1326, s1362
Mucha M. s1139
Mueller A. s1243
Mueller H. s1199
Mueller T. s1295
Muhler M. s1226
Müllen K. s1228, s1271, s1333, s1360, s790, s800
Müller C. E. s715, s853
Muller J. s894
Müller K. s639
Müller M. s1082
Müller P. s1265
Müller T. J. J. s699
Münch A. s1202
Munoz-Fernández M. A. s787
Murai K. s1202, s1208
Murakami S. s1179
Murashima T. s899
Muratov D. s1232
Muresan L. E. s1196
Muromachi S. s691
Murray B. s1243, s1244
Musa S. s1062
Muscarella M. s1167
Mushtakova S. s617
Musolino M. s1343
Mustafa M. Hd. Rais s954
Musumeci R. s722
Mutaliyeva B. s1062, s929
Mutti F. G. s802
Muzafarov A. s1323
Muzart J. s1361

N

Nachon F. s1068
Nadaroglu H. s907, s908, s908, s914, s918
Naderi H. s1080
Nadri S. s1213, s941
Naffrechoux E. s662
Nagendiran A. s1097
Naglah A. s1106
Nagy B. s1186
Nagy T. s1357
Nagy T. Z. s1314
Nakagawa T. s1208

Nakamura H. s1006
Nakano S. s899
Nakayama K. s1063
Nakazawa C. s1048
Nalbantoglu F. s1244
Nam H. s1127
Nam S. C. s1173, s1176
Nam W. s685
Nanni D. s1220
Narita A. s1333
Nariya B. s850
Nassar M. s1063
Nastova I. s1245, s873
Nasun- Saygili G. s647
Natour S. s1064
Nau W. M. s869, s887
Naumkin F. s1245, s873
Navratil R. s1295
Navratil T. s646
Nechab M. s771
Negro C. s914
Neier R. s1033, s767
Nemec I. s934
Nemec M. s921, s922, s923, s928
Nemecek J. s1064
Nemeckova A. s1139
Nemes G. s1344, s997
Nemeth B. s854
Nemeth J. s1065
Neo S. S. s814
Neouze M. s845
Neouze M. A. s1200
Neri D. s796
Neuburger M. s996
Neufeld K. s1203, s707
Neufuss S. s921, s929
Neumann M. s1031, s608, s970
Neumann T. s704
Neves A. C. B. s1337
Neves R. s651
Ng C. H. s954
Ng S. W. s954
Nguyen B. T. T. s608
Nickovic S. s907
Nicolescu A. s1282, s1336
Nielsen C. J. s863
Nielsen J. L. s693
Niemi J. s1358
Niewiadomski P. s868
Nikitenko S. s662
Nikitina V. E. s652
Nikolaev A. s1334
Nikolic J. s1065, s1334
Nikolic N. s1076
Nischan N. s967
Nishiura Y. s775
Nitschke J. R. s733
Nocito F. s692
Noe C. R. s1077
Noel T. s1273, s762, s801
Nogueira I. s651
Noh T. H. s961
Nolte R. s731
Norcliffe J. s1280
Nordmeyer D. s1246
Norgaard K. s1237, s1246
North M. s661
Noseck U. s922
Nöske R. s970
Novák M. s622
Novak P. s727, s855, s892
Novák Z. s1290, s1314, s1349, s1357
Novakova V. s1279
Novakova Z. s1066, s1247
Novosad J. s1236
Novotná R. s935
Novotny V. s1140
Nsouli N. s989
Nunes C. D. s963, s978
Nunes T. G. s963
Nunes Y. s1240, s1255
Nunez A. s1096
Nurullah S. s1148
Nuryyeva S. s1425
Nyholm L. s596

O
Obsil T. s891
Obsilova V. s891
Oca M. L. s1141
Occhiuto I. s1216
Odell B. s807
O’Donoghue A. s782
O’Donoghue A. C. s1317
O’Donovan L. s726
Ochoa-Puentes C. s884
Oeckler O. s851, s852
Oh J. M. s1168
Oh T. s1335
Ohlendorf G. s1335
Ohlmann D. M. s1268
Ohmura R. s1174, s659, s662, s691, s818
Ohnishi-Kameyama M. s1229
Ohta T. s1063
Ohtaki K. s1179
Oja T. s1358
Okamoto S. s1066
Okamoto Y. s1056
Oklestkova J. s777
Olejnickova J. s1170
Olejniczak A. B. s1006
Oleko A. s906
Oliveira A. s1161
Oliveira J. s874
Oliveira-Brett A. M. s598
Oliver R. s1094
Olson A. s704
Ölzer E. s1126
Omastova M. s1247
Omtvedt J. P. s928
Omurtag P. S. s1067
Ondel Eymin M. J. s1060
Ondruschka B. s656, s821
O’Neil G. s593
Onganer Y. s1111, s1112, s1112, s1113, s1113, s1115
Onjia A. s1152
Oprea O. s1195
Oprescu E. E. s1177
Orbay A. s1142
Ordonez A. s926
Orekhova N. s1171, s1219, s1248
Orenes R. A. s1272

Oreshkin I. s1171
Orinak A. s1256
Orinakova R. s1247, s1256
Orlanducci S. s1216
Orlov A. s1038
Orlovic S. s911
Oro L. A. s694
Ortega L. s948
Ortgies D. s1067
Ortiz M. C. s1141, s616
Orvig C. s983
Osako M. s636
Oscarsson S. s806
Ostrand-Rosenberg S. s728
Ostrovskii O. s901
Osuna S. s823, s865
Osz K. s649
Otte P. s1068
Otto S. s780
Otyepka M. s872, s876
Ouali A. s1336
Ouchaou K. s1187
Oueis E. s1068
Öz S. s1142, s1149
Ozbas F. s915, s915
Ozbek M. s1244
Ozden T. s1244
Ozerov A. s901
Ozgen O. s915, s915
Özkaramete E. s1142, s610
Özkinali S. s1069

P

Pabisch S. s993
Pabst A. s1069
Pace A. s1255
Pacchioni G. s822
Pacha-Olivenza M. A. s1251
Pache A. s1203, s961
Pacheco M. J. s647, s906, s916
Paczkowska M. s895
Paesani F. s1242
Palcut M. s1203
Palermo C. s1167
Palm G. J. s687
Palmas P. s1143
Palmgren P. s806
Palmieri A. s655
Palszegi T. s827
Panacek A. s1219, s1231, s1234, s1257
Pandey G. s1041
Pandiyarajan C. K. s792
Pansu R. s802
Panteleitchouk T. s1120
Panyala N. R. s1110
Panzer R. s1070
Paolella S. s726
Papastefanou C. s673
Papic P. s645
Papouskova B. s1143
Pappalardo L. s1132
Paradas M. s771
Paradies J. s1070, s1071
Paraschivescu C. s1336
Parastar H. s618
Parchmann I. s632
Parella T. s975
Paria S. s1074
Park A. s1332
Park H. K. s1134
Park H. Y. s1167
Park J. s937, s972
Park J. H. s1177
Park J. W. s1163
Park K. s1176
Park N. s1071
Park S. s1163, s1184
Park S. J. s1168
Park S. K. s1165
Park Y. s926
Parker J. s672
Parker S. C. s996
Paruch K. s1313, s1323
Parviainen A. s641
Parvu M. s885
Parvulescu V. s1092
Parvulescu V. I. s1191
Pasdar H. s986
Pasfield L. s1337
Pasquinet E. s1143, s802
Pasta M. s594
Pastori N. s767
Pastva J. s976
Pasztor-Huszar K. s677
Patarin J. s849
Patrick T. s1016
Pauk V. s1143
Paulikat M. s871
Paulus F. s1246
Pavel O. D. s1092, s1186
Pavlath A. s629
Pavlista M. s1206
Pavlov G. M. s1102
Pavlychev A. A. s830
Pavoni B. s912, s913, s913
Pawlicki M. s1072
Pechyen C. s1072, s1248
Peckova K. s1130, s597
Pedroso De Lima M. C. s791
Peh A. E. K. s608
Pehlken C. s947
Pejic N. s1144, s1160
Pejov L. s873
Pejova B. s1245
Pekker S. s1235, s1249
Pellecchia C. s687
Pelloux H. s714
Peluso P. s1055, s1055
Pena-Mendez E. M. s1110
Pennell M. s1073
Pereira E. s651
Pereira M. M. s1198, s1333, s1337
Pereira R. s909
Peretz S. s1269
Perevyazko I. s1102
Perhaita I. s1196, s1344
Perin J. L. s792
Perinka N. s1338
Perlikova P. s1073
Perman J. s1218
Perrier A. s1336
Perutz R. N. s996

Peruzzini M. s665, s679
Peschel L. s715
Peter K. s1263
Petermann L. s976
Peters W. K. s829
Petersen J. s817
Petho B. s1290
Petkovic S. s866
Petr J. s1144, s930
Petrar P. s997
Petruzelka L. s1154
Petukhov A. s818
Petukhova N. s818
Petunin P. s1317
Petzinger E. s902
Peuchmaur M. s714
Pezron I. s780
Pezzella A. s728
Pezzolesi L. s1178
Pfaffeneder T. s1082
Pfeffer J. s802
Pfirrmann S. s688
Pfitzner A. s1031
Pfleiderer S. s1249
Pflieger R. s662
Pfund E. s1050
Phetsang W. s890
Philippot K. s1198
Phulwale B. V. s1328
Piarulli U. s700
Pidchenko I. s922
Piehler T. s1030
Piekarska B. s897
Piemontesi C. s813
Pietruszka J. s1274, s1286, s707, s778
Pievo R. s1241
Pigeaux M. s1338
Pignataro B. s1217, s1255, s712, s744
Pilard J. F. s1007
Pilnacek K. s1090
Pilsl L. s1074
Pilz D. s976
Pinakoulaki E. s1165
Pingoud A. s902
Pinheiro L. s874
Pintado M. s1161
Pinter B. s917
Pinto A. P. s1137
Pinto D. C. G. A. s1001
Pinto I. S. S. s1187
Pinto J. s1339
Pinto M. s718
Pinto V. s793
Piot C. s924
Pipelier M. s1001
Pirtsch M. s1074
Pivesso P. s1175
Pivetta T. s1110
Pivodova V. s895
Piwowar M. s877
Pizzo F. s663
Plain J. s1262
Plasser F. s781
Plenge J. s729, s877
Plutino M. R. s940
Podobedov R. s981
Poeta P. s1159
Pohl R. s1298
Poisson G. s1075, s621
Poisson J. F. s1010
Pokorny K. s939
Polinskaya M. s1214
Polivkova M. s930
Pombeiro A. s683
Pompach P. s892
Ponomarenko S. s1214, s1323
Popov S. s1152
Popovic B. s911
Popovic M. s901
Popovici E. J. s1196, s1344
Popp A. s1089
Popp J. s699, s781, s826, s830, s862, s893, s988
Popsavin M. s1020
Popsavin V. s1020
Pori M. s1289, s722, s777
Porsch T. s694
Posa M. s875, s875
Pospisil L. s1424
Pospisil P. s643
Postils V. s820
Postnikov P. s1317
Potopnyk M. s1075
Pototschnig G. s1339
Pöttgen R. s932
Pouget C. s1021
Pour M. s1315
Powell A. K. s933
Pozdeev O. s1042
Pozzo P. D. s726
Prado Varela A. F. s761
Prandi B. s726
Prato M. s739
Prats Montalban J. M. s617
Prchalova E. s1076
Prekodravac B. s1076
Presser A. s1059
Pretorius R. s945
Prikaznov A. s942
Prikryl J. s1206
Primo A. s658
Privalov T. s1173
Procházková E. s1077
Prodi L. s749
Proisl K. s1340
Prokop A. s1102
Prosperini S. s767
Proust A. s1239, s681
Prucek R. s1219, s1234, s1257
Prusty D. K. s796
Pryanichnikova A. s929
Puchberger M. s993
Puchta R. s686, s883, s939, s949, s958
Puetz K. s1145
Pujol A. s737
Pulido D. s787
Punta C. s767
Putala M. s1019, s798
Putun A. E. s1193
Putun E. s1193
Pykal M. s868, s876
Pyykko P. s813
Queva S. s1077

Quignard F. s1091, s1187, s658
Quintanilha A. s668

R
Raboch J. s1154
Rac V. s1199
Radeka M. s1188, s1194
Rademann K. s1256, s752
Radenkovic N. s1312
Radic N. s1145
Radojevic I. s950
Radtke V. s1145
Radu A. s1177
Raduly I. s1188, s643
Raduly L. s1188, s643
Raessler M. s601
Rafiee E. s1213, s1230, s1250, s1250, s941
Raindl J. s922
Rajacopal B. s884
Rajakovic L. s1152
Rak J. s896
Rakic V. s1199
Ramadan A. s997
Rambousek L. s1301
Ramos-Cordoba E. s876
Rampazzo E. s749
Rampazzo G. s912, s913
Ranc V. s1219
Ranca A. s1166
Ranogajec J. s1188, s1194
Rapantova N. s643
Rarova L. s1101, s777
Räsänen M. s845
Raschpichler C. s877
Rasmussen K. s880
Rastelli G. s1068
Rasulova N. s1323
Ratajczyk T. s1340
Rau S. s1146, s1352, s699, s830, s862, s943, s944, s947, s976, s988
Rauch G. s1078
Rauch-Kröhnert U. s1246
Raymo F. s750
Razic S. s600
Reale S. s728
Reany O. s797
Reau R. s747
Reck L. s1078
Reddy K. R. s1046
Redey A. s1188, s643, s917
Redini F. s1000
Reeh P. s1331
Reetz M. T. s589, s589
Reich T. s638
Reinoso S. s1203, s961
Reis M. s874
Reiser O. s1017, s1036, s1041, s1045, s1053, s1074, s1074, s1180, s1309
Reissig H. s1271, s1364
Reissig H. U. s1051
Reiter C. s1079
Remko M. s898
Renard P. Y. s1068
Renaudineau S. s1239
Repovsky D. s827
Resch-Genger U. s612, s903
Resnati G. s836
Resongles E. s644, s924
Respaud M. s1240
Retegan T. s928
Reutenauer P. s1360
Rezabkova L. s891
Rezaei M. s1210
Rezanka M. s768
Rezanka P. s1135
Rezinkova Y. s981
Reznik V. s1334
Rgaard K. N. s1229
Riala M. s1079, s799
Ribagorda M. s740
Ribas X. s1222, s701, s951, s955, s975
Ribeiro A. E. s1159
Ribeiro T. s748
Ricci A. s1091
Ricci L. s1058
Richards R. s1251, s660
Richards R. M. s1191
Richardt G. s1330
Richarz R. s1292
Richel A. s1191
Richert C. s891
Richmond C. s1254
Richter C. s1246
Rico M. s1223
Rieger J. s1319, s792
Riemer M. s1080
Riezman H. s999
Riisiö A. s962
Rinfray C. s1239
Rioux S. s1067
Rissanen K. s1008, s1035, s1093, s1234, s1324, s953
Riva S. s706
Rizk H. s1017
Roberts D. s1151
Robitzer M. s1091, s1187, s658
Rocha D. H. A. s1001
Rocha G. s658
Rocha-Santos T. s1120, s1221, s609, s909
Rochat S. s1341
Rochefort D. s1116, s594
Rockstroh N. s1352
Rodriguez J. s768
Rodriguez Moran J. s1289
Rodriguez Perez L. s741
Rodríguez-Cano A. s1251, s1252
Rodríguez-Márquez I. s771
Roeder A. s896
Roehr M. s817
Rogerson M. s645
Roh J. s1037, s1064
Rohovec J. s646
Rohwer L. s695
Roithova J. s1351
Rollet M. s770
Romano-Rodriguez A. s1213
Romeo A. s1216, s1252
Romero A. s1242
Romieu A. s1068
Rominger F. s1007
Roncali J. s773
Ronchin L. s1191

Ronco C. s1068
Roost C. s1341
Rosa P. s980
Rosado M. T. S. s1204
Rosatella A. s783
Rosca P. s1177
Rosca S. s1160, s1166
Rose N. s898
Roseiro T. s1204
Rosenthal T. s851, s852
Rosnes M. H. s1253
Rossi B. s767
Roterman-Konieczna I. s877, s897
Roth K. s670
Röttger Y. s896
Roubeau O. s680
Rouchal M. s1275
Rouden J. s1338
Rouessac V. s802
Roullin G. s1214
Rousseau T. s773
Rousselin Y. s936
Roux A. s999
Roux S. s607
Röver I. s964
Rovira C. s835
Rovisco A. s1240
Royer S. s1196, s1197, s1197, s1207
Royo M. s787
Rozati S. M. s657
Rozbesky D. s855
Rudic O. s1188, s1194
Rudic S. s807
Rudolf O. s1342
Rudolf P. s809
Rudroff F. s707
Ruecker H. s897
Ruehl E. s830
Rueping M. s1310
Rüffer T. s962, s989
Ruggeri G. s1058
Rühl E. s1246, s729, s877
Ruhlmann L. s1319
Ruiz De La Oliva A. s1254
Ruiz Sierra G. s1116
Rukk N. s991
Rulisek L. s1021
Rumlova T. s1146
Rupar P. s954
Rutjes F. s719
Rutledge D. s615
Rutter J. s846
Ryabov A. s683
Ryakshina A. s902
Rybarska J. s897
Rybina A. s882
Rybinova M. s1147
Rydchuk M. s1171
Rychlovsky P. s1147, s605
Ryslava H. s1136

S
Sabata S. s1351
Sabot C. s1068
Sabry N. M. s1265
Sacchetti A. s1342, s1343
Sachdev H. s1228
Sacinti C. s1128
Saez Araoz R. s1222
Safi B. s1138, s1253
Safi J. s1262
Safi Shalamzari M. s725
Sagar R. s807
Saglam B. s1343
Sahin O.I. s1161
Sahoo D. s723
Saidi M. s1138, s1147, s1253
Saidulu G. s1046
Saka E. T. s986, s987, s987
Sakac M. s1076
Sakai N. s1347, s800, s999, s999
Sakamoto H. s662
Sakamoto J. s1320, s1346, s747
Sakamoto Y. s840
Salbu B. s928
Salice P. s1255
Salisova M. s898
Salle M. s798
Salmi M. s681
Salon J. s770
Salvador P. s876
Salzer R. s606, s625
Sama J. s1213
Samal M. s1121
Samide A. s1118, s1119
Samori C. s1178, s659
Samori G. s1178
Samori P. s743
San Felices L. s1203, s961
Sanchez D. M. A. s1286
Sanchez L. s794
Sánchez M. I. s711
Sánchez M. S. s616
Sanchez S. s679
Sanchez-Martin R. M. s1307
Sanchez-Nieves J. s787
Sandberg M. N. s812
Sanli N. s1109, s1140, s1141
Sanli S. s1109, s1140, s1141, s1148
Sans Sangorrin V. s1254
Santos L. M. N. B. F. s1339
Santos P. V. F. s598
Santos S. s874
Saoudi A. s906
Saponar A. s1344
Saptalena L. G. s1148
Sarabia L. s1141
Sarabia L. A. s616
Saraiva M. S. s963
Sarap N. s1144
Sarbu C. s674
Sarbu L. s905
Sarek J. s722
Sarjadi M. S. Sarjadi s790
Sarreshteh Dari Z. s1080, s1344
Sarris J. s943
Sartorio C. s1255
Sashuk V. s746
Sasson Y. s664
Sattasathuchana T. s878
Sattler D. s990
Sattler J. s802

Saulnier S. s1345
Sautet P. s823, s824
Sauve S. s648
Savoia D. s767
Savonina E. s1149, s603
Sayikli C. s1150
Sazelova P. s604
Sberveglieri G. s1172, s657
Scamporrino E. s1060
Scanlan E. M. s807
Schaefer T. s705
Schaefers F. s1292
Schaeffer G. s1081
Schäfer J. s704
Schaller G. s1081
Schalley C. A. s1093, s1233, s1234, s990
Scharnweber D. s705
Schatz J. s1193, s1290, s1331
Schatz P. Of. Dr. Juergen s1190
Schaumberg C. s1256
Scheblykin I. s781
Schedler U. s612
Scherf U. s789
Scherman O. A. s869
Schettino V. s839
Scheurer A. s939
Schiesser S. s1082
Schildbach D. s985
Schiller A. s1118, s1122, s611, s685, s861, s946, s957
Schindler S. s1087, s684, s977
Schinkel M. s1082
Schlesiger D. s1316
Schlesinger M. s881, s962
Schleyer P. V. R. s1322
Schlüter A. D. s1262, s1320, s747
Schlüter D. s1346
Schmeide K. s639
Schmeisser M. s939
Schmid W. s1009, s1084, s998
Schmidbauer S. s1028, s1083
Schmidt B. s1018, s1023, s1048, s1080, s774
Schmidt D. s1293, s965
Schmidt R. s656
Schmidtchen F. s1099
Schmitt F. s968
Schmitt M. s988
Schmitt Y. s699
Schmitz D. s1032, s1083
Schmitz P. s1348
Schmölzer C. s1084
Schnabel M. s1320
Schnakenburg G. s1335
Schneider M. s650, s852
Schneider M. W. s799
Schneider R. s1235
Schneider S. s887
Schnorr J. s1246
Schnorr J. M. s612
Schnürch M. s718
Schoen J. C. s851
Schöffmann A. s718
Schofield C. s898
Scholz F. s1424
Schönfelder N. s1348
Schreiner P. R. s1085, s1298, s853
Schröder D. s1155, s1295
Schröder H. s1234
Schroder M. s847
Schröder T. s851, s852
Schroll P. s1084, s1286
Schröter P. s968
Schubert U. S. s1102, s1102, s1201, s1217, s1236, s1293, s781, s849, s964, s979, s982, s993
Schuler S. M. M. s1085
Schulz S. s947
Schulz T. s1036, s694
Schumm B. s1125
Schuster T. s789
Schütt C. s878
Schütz S. s699
Schwartz T. s746
Schwarz H. s591
Schwarz T. s718, s977
Schwarzer A. s689, s973
Schwedtmann K. s960
Schweez C. s1085
Schwegmann H. s909
Schwendt P. s956
Schwenzer B. s1233, s705
Schwikowski M. s637
Scopelleti R. s932
Scott L. T. s1281
Sebastian R. s1345
Sebastiani D. s1330
Sebej P. s1265
Sebela D. s1170
Sebenyi A. s875, s875
Sebesta F. s635, s922, s923
Sedlak D. s1076
Seeman N. s834
Segler S. A. W. s1054, s772
Seidel F. s1221
Seifert A. s955
Seilerová L. s1204
Seitz O. s1367
Seitz W. s739
Sekirnik R. s898
Sellevag S. R. s863
Sells D. s733
Sem D. s704
Sembera F. s764
Semenov V. s1334
Semioshkin A. s942
Semisch A. s1246
Sen F. s1181
Sen S. s1181
Senf A. A. s1233
Seng H. L. s954
Sengupta S. s812
Senila M. s644
Seniori S. s679
Senocak N. s1149
Seo B. s1134
Seo Y. s1335
Seong R. s1164
Sepelak J. s827
Septelean R. s997
Sepúlveda A. E. s682, s1223
Serdaroglu E. s830
Serein-Spirau F. s802
Sério S. s1240, s1255

Sermon P. s1205, s852
Serpell C. s730
Serra I. s931
Serrano E. s1223, s682
Serrano-Plana J. s955
Serrya R. s721
Servalli M. s1346
Servusova B. s1346
Sesalan B.S. s969
Sessler M. s1190
Setnicka V. s1130, s1154
Sevcik J. s1144
Sevcik R. s944
Severin K. s932, s937
Sevim A. M. s957
Sezgintürk M. K. s1150
Sforazzini G. s1347
Sforza S. s1168, s709, s726
Sfriso A. s913
Sgarbi E. s1168
Shaban S. s997
Shaffer C. s1295
Shaheen K. s1347
Shaik S. s819
Shakeri M. s806
Shames A. s958
Shamsiev R. s991
Sharafutdinova D. s1334
Shaw S. s903
Shen J. s1056
Shepherd H. s820
Sheppard T. s1050, s1073
Sherina N. s1110
Shevchenko N. s721
Shibata M. s1205
Shilun Q. s842
Shimamura A. s975
Shimizu G. s843
Shimizu M. s765
Shimizu T. s1238
Shin D. W. s1168
Shin J. H. s1127, s1134
Shiotsuki T. s893
Shishilov O. s981, s984
Shmatova E. s901
Shoyele S. s1257
Shtykov S. s607
Shubely M. s1258
Shubina T. s695
Si Z. s1424
Sidebottom A. s716
Siegel J. S. s1266, s1276, s1281, s1341, s858
Siemeling U. s694
Sierra C. A. s1286
Sierra Ramos A. F. s1286
Sigmund E. s1348
Silaghi-Dumitrescu R. s674, s884, s885, s888
Silaghi-Dumitrescu L. s997
Silha T. s934
Sillanpää R. s962
Silva A. s1288
Silva A. M. G. s1339
Silva A. M. S. s1001, s1057, s1086, s1339
Silva L. s1120
Silva L. C. s1255
Silva M. R. s1204
Silva Pereira M. I. s1137
Silva S. s879
Silva S. G. s791
Silva V. s1288
Silva V. L. M. s1057, s1339
Silvani A. s1343
Silvestrin S. s1172
Silvi S. s1211, s1211, s734
Sima M. s644
Simak O. s1354
Simandi B. s1190
Simao C. s835
Simeonov S. s783
Simko D. s1357
Simon A. s1281
Simon G. s917
Simon P. s677
Simon R. C. s1274
Simon Rubio L. s1289
Simon Sarkadi L. s620, s677
Simons J. P. s807
Simsir H. s1012
Simunek P. s1009
Sin D. W. M. s1162
Sinai A. s1349
Sindelar V. s1296
Sindelár V. s1356
Sinha K. M. s797
Sinn S. s861
Sipek M. s1090
Sisa M. s1350
Siva Pereira M.I. s1240
Skach K. s1350
Sivaev I. s942
Skalova L. s1132
Skantarova L. s1256
Skapin T. s873
Skarnemark G. s928
Skeríková V. s599, s1153
Skipperud L. s928
Skorpilova L. s1086
Skriba A. s1351
Skrivanj S. s1152
Skryabina A. s991
Skudas R. s613
Skuterud L. s636
Skvorova L. s1135, s1146
Slanina T. s1265
Slaninova J. s724, s886
Slavícek J. s1351
Slavik P. s1352
Slavíková B. s778, s1301
Sleiman H. s730
Slovak V. s1189, s1192
Slovakova K. s1151
Slugovc C. s846
Smejkal P. s927
Smith A. s622
Smith C. I. E. s712
Smith N. W. s600
Smith S. s1053
Smulders M. M. J. s733
Smyth S. A. s648
Snauwaert H. s1002
Soares H. M. V. M. s1187
Sobota M. s810

Socher E. s889
Socoteanu G. M. s1189
Sodre J. R. s1178, s653
Soin A. s1149
Sokolowski K. s690
Sola M. s701, s820, s823, s865, s870, s871
Soldati R. s1289, s777
Solinova V. s604
Sollogoub M. s1239
Soltys K. s690
Somogyi V. s1188, s917
Söncksen L. s936
Song J. H. s1185
Soni R. s758
Soos T. s1029, s1097, s1361
Soós T. s1329
Sormaz M. s1077
Sormova K. s605
Sorsche D. s1352
Sortino S. s751
Sorus M. s733
Sostaric I. s600
Söthje D. s1015
Sotolar R. s1170
Soukup J. s1151, s599
Soulard M. s849
Sousa E. s718
Sousa I. s874
Sousa J. L. C. s1086
Sousa M. s1212
Souza P. s653
Soydaner U. s996
Sozzani P. s1195, s834
Spampinato S. s720
Speicher A. s1325, s1348, s1353
Spencer A. P. s829
Spendlikova I. s922, s923
Speranza V. s787
Spies S. s891
Spiess H. W. s1330
Spiridon M. C. s1034
Spirina J. s1209
Spitaleri F. s1060
Spivakov B. s603
Spiwok V. s872
Sponer J. s872
Spork A. P. s1318
Squizzato S. s912, s913
Sredovic I. s1152
Sreedhar B. s1309
Srinivasan A. s1257
Srinivasan S. s611
Staehle R. s944, s976
Stajner D. s911
Stangenberg R. s790
Stanglmair C. s1087
Stanisic S. s1152, s866
Stanislav M. s1359
Stanislawski B. s613
Stanková M. s599, s1153
Stara I. s1121
Stark W. J. s1036
Stary I. s1121
Stastna K. s635
Staubitz A. s1054, s1297, s1355, s772
Stavarache C. s1359
Stefaniuk A. s1353
Stefano C. s938
Stefanovic O. s950
Stefan-Van Staden R. I. s598
Stefelova J. s1189
Steier P. s923
Stein A. s840
Steinbach J. s709, s715, s717, s889
Steinbach M. s1087
Steinborn D. s989
Steinborn M. s983
Steiner G. s606
Steinhart H. s672
Steinke N. s1123
Steinkellner G. s705
Steinmann S. s813
Steinnes E. s636
Stejskal F. s1354
Stejskal J. s1338
Stenclova P. s1088
Stenclová Z. s1119
Stepan E. s1177
Stepanek M. s891
Stepanek O. s1088
Stepanek P. s1354
Stephan H. s709, s715, s715, s717, s889
Steudtner R. s639
Steunenberg P. s785
Stibor I. s1094, s764
Stiborova M. s866
Sticht H. s710, s889
Stierand P. s920
Stiewe C. s852
Stinga G. s1034, s1034, s1268, s1269, s1355
Stirling A. s1357
Stoddart J. F. s1211
Stogniy M. s942
Stochel G. s945
Stojkovic J. s645
Stolarikova J. s1037, s1064
Stolle A. s656, s821
Stolper T. s879
Stopa B. s897
Stopa G. s945
Stoppioni P. s665, s679
Straka J. s724
Strassner T. s1036, s959, s960, s967
Strauch P. s970, s973
Strbanova S. s621
Streb C. s701, s974, s981
Streifinger B. s1089
Streit H. C. s952
Strianese M. s687
Strizik L. s1206
Strle G. s769
Strnad M. s777
Strohmann C. s985
Stromme M. s925
Strueben J. s1355
Studer A. s1013
Studzinska S. s1115, s857
Stufano P. s693
Stumpf P. s1246
Stündel A. s896
Sturala J. s1356
Sturla S.J. s1011

Stutz C. s749
Stutz Yaunner R. s761
Stylianou M. s1169, s686
Styskalik A. s1236
Suchomel P. s1257
Sudy B. s880
Sugimoto N. s899
Suginaka T. s662
Sugiyama H. s708
Suh S. K. s1163
Sukenik C. s1210, s1258
Sukenik C. N. s1224
Sukhov B. s721
Suksi J. s922
Sulc M. s727, s891
Sulovsky P. s1143
Sun B. s678
Sun J. s1174
Sun Y. s740
Sun Z. s1103
Suptil J. s662
Surin N. s1214, s1323
Suss-Fink G. s678
Sustekova J. s1089
Sutyagina E. s818
Suzen S. s1153, s899
Suzuki R. s893
Svec F. s599
Svec J. s1356
Svehlakova T. s722
Svoboda I. s1142, s1149
Svoboda J. s1088, s881
Svobodova H. s833
Swager T. M. s1341, s612
Swart M. s823, s865
Swarts J. s974
Swarts P. s974
Sykora J. s1352
Symes M. s666, s999
Symes M. D. s1253
Synooka O. s1293
Synowiecki M. s1179
Synytsya A. s1154
Sypaseuth F. D. s1285
Syrovy T. s1338
Sysel P. s1090
Szabo F. s1357
Szabó F. s1290
Szabo J. s917
Szabo Nagy A. s917
Szabo O. s886
Szantay C. s1361
Szecsenyi A. s1190
Szekely E. s1190
Szemmelveisz K. s912
Szidat S. s637
Szilvagyi G. s1357
Szoecs V. s827
Szpilman A. s757
Szterenberg L. s1072
Szulmanowicz M. s696
Szumna A. s794
Szuppa T. s656
Szyfter K. s1425

T

Tabouche A. s919
Tachikawa S. s1006
Taddia M. s627
Taft H. s675
Tagliavini E. s1178, s1181, s659
Tahtinen P. s1358
Tai C. W. s1097, s806
Takahashi T. s1327, s775
Takahashi-Umebayashi M. s999
Takeya S. s691
Talinli N. s1022, s1023
Tan K. s954
Tan S. W. B. s1090
Tanaka H. s775
Tanaka K. s1258
Tanchoux N. s1091
Tang Y. s863
Tanyeli C. s774
Tanzer E. M. s1091
Taraba B. s1192
Tarabek J. s1155
Tarabová D. s1092
Taran F. s1187, s658
Tarko L. s1359
Tarnowska K. s1425
Tase A. s893
Tasgin E. s907, s918
Tasic A. s866
Tatarkovic M. s1154, s1154
Tateishi-Karimata H. s899
Tauber K. s802
Tauler R. s618
Taupitz M. s1246
Tavares D. S. s651
Taylor J. s843
Tecimer M. A. s1284
Tedeschi T. s1168, s709, s726
Teixeira J. A. C. s1339
Telgheder U. s1148
Tellkamp T. s1358
Temprano I. s808
Tenne M. s959
Tenora L. s1359
Teodorescu F. s1092, s1359
Terasaki O. s840
Terraneo G. s836
Terryn C. s1214
Teslyar G. s1114
Tettenborn O. s628
Teusch C. s1360
Thalhammer A. s898
Thanakkasaranee S. s1072
Thiedemann B. s772
Thiel W. s816
Thiel W. R. s699
Thiele T. s612
Thies S. s878
Thomas C. M. s788
Thomas S. s761
Thorring H. s636
Thorwirth R. s656
Thumann S. s1290
Thurner A. s1274

Tian Y. s1103, s1103
Tiao H. C. s1201
Tiburcio J. s1225, s1242
Tichy M. s1093
Tiersch B. s970
Timári G. s1314
Tirayut V. s1094
Tisovsky P. s857
Tißler A. s805
Toader M. s1221
Todasca C. s1160, s1166
Tognetti V. s1068
Toh C. S. s608
Tokuda H. s1347
Tölle K. s1226
Tolomelli A. s720
Tomasek J. s1190
Tonetti C. s726
Toolaram A. P. s650
Topic F. s1093
Toprak M. s1112
Torabi F. s918
Torri C. s659
Tóth E. s933
Toth K. s1281
Toughrai S. s792
Trabolsi C. s1425
Trader D. s716
Tran D. N. s1075
Traoré M. s714, s803
Trávnícek Z. s934, s935
Trewin A. s1206, s820, s844, s848
Trifunovic J. s875
Trifunovic S. s950
Triggiani M. s1166
Trinca L. s1266
Triska J. s1170
Trmcic M. s1280
Trnka T. s822
Troff R. W. s1093
Tronnier A. s967
Trusova M. s1317
Truss M. s1082
Trzeciak A. s696
Tsaousi K. s1169, s673
Tschammer N. s1049
Tschan M. s788
Tschierlei S. s988
Tsien R. Y. s590
Tsikin A. s617
Tskhovrebov A. s937
Tsogoeva S. B. s1024, s1079
Tsuboi M. s1232
Tsuchiya H. s1170
Tsuchiya W. s893
Tsybin Y. s602
Tsybizova A. s1155
Tucek J. s1234
Tuczek F. s936, s938
Tucher J. s981
Tudose M. s1189, s1268
Tugarova A. V. s652
Tunca U. s1067, s998
Tuncel D. s750
Tundo P. s661
Turano P. s900
Turczel G. s1313
Turebekova G. s1180
Turecek F. s723
Turel I. s684
Turgut Y. s1094
Turner P. s1073
Tutino M. s916
Tvaroska I. s822
Tyurenkov I. s901
Tzanis L. s849
Tzeng B. C. s969
Tzschucke C. C. s1285

U
Uckardes H. s991
Uckun Z. s1153
Ugalde J. M. s871
Ugur M. H. s1106, s1107
Uhlir J. s928
Ulbrich K. s1094
Ulrich S. s1095
Ulrichova J. s1307, s895
Unciti-Broceta A. s1307
Unger Y. s959
Ungureanu A. s1196, s1197, s1197, s1207
Unkelbach C. s985
Unold J. s1095
Urankar D. s1340
Urban E. s1077
Urban J. s1153
Urbaniak P. s1046
Urner L. s1360
Uroos M. s703
Urtiaga M. K. s1207
Ussawadilokrit A. s1248
Utasi A. s643
Utczas M. s1190
Uygun O. s1150

V
V V S R. P. s900
Vaccaro L. s663
Vacek J. s1158
Vaden T. D. s807
Vafaie Sefti M. s1080, s1344
Vagfoldi Z. s725
Vaidhyanathan R. s843
Valasek M. s1259, s764
Do Vale M. L. C. s791
Valentin L. s684
Vales K. s1301
Valla C. s1077
Valla J. s654
Van Berkel S. S. s1275
Van Boekel M. s671
Van Der Eycken E. s785
Van Der Eycken J. s1002, s1273, s762
Van Der Lee A. s802, s844
Van Der Westhuizen B. s974
Van Der Westhuizen J. s630
Van Der Zant H. s736
Van Eldik R. s690, s883, s939, s945, s949, s958, s997
Van Gulick L. s1214
Van Jaarsveld N. s972
Van Leeuwen F. s720, s785
Van Rooyen P. s1208

Van Staden J. F. s598
Van Staden J. K. F. s596
Van Staden R. I. s596
Vandentorren S. s906
Vandyck K. s762
Vanek J. s1155, s944
Vanek V. s894
Vanthuyne N. s771
Vantomme G. s1096
Vaquero J. J. s1096
Varella E. s624, s624
Varga E. s1097
Varga S. s1361
Vargas Jentzsch A. s800
Vasheghani-Farahani E. s1344
Vasile A. s1188
Vasile B. s1195
Vasilescu D. S. s1034
Vasold R. s1028, s1083
Vass E. s1357
Vass I. s917
Vasseur A. s1361
Vavasori A. s1191
Vavrova K. s1037, s1064
Vaz P. D. s978
Vázquez M. E. s711
Vázquez O. s711
Vazquez-Gonzalez A. M. s925
Vecer J. s891
Veciana J. s835
Vega L. F. s666
Veinot J. s742
Veinot J. G. C. s1227
Vejsová M. s1305
Velders A. s785
Veldkamp B. s828
Velic D. s627, s827
Ventura C. s874
Ventura K. s1124, s1131
Venturi M. s1211, s734
Verho O. s1012, s1097, s806
Vermesan H. s1118
Vermeylen R. s725
Verrier C. s1010
Very T. s821
Verziu M. s1191
Vesela P. s1192
Veszprémi T. s854
Vetchinkina E. P. s652
Vetulani J. s631
Veverkova L. s1159
Viau L. s1287
Vicente A. A. s1339
Viceriat A. s1010
Vícha R. s1275
Vickers C. s703
Vida N. s1101
Vidal K. s948
Videnska K. s923
Viehweger K. s717
Viel S. s770
Viers J. s644
Vilar R. s713
Vilcekova Z. s934
Vilhelmsen M. H. s1098
Villafane F. s985
Villani V. s880
Villegas C. s739, s741
Vincze-Csom V. s643
Vineis C. s726
Vins P. s1362
Viola A. s720
Vioux A. s1287
Visa A. s1326, s1362
Visin F. s913
Viswambharan B. s1363
Vitvarová T. s881
Vives G. s1259, s735
Vladimir S. s1154
Vlaisavljevic S. s901
Vlasiou M. s673
Vlasov V. A. s652
Vlk M. s722
Vo H. T. s1182
Voburka Z. s724
Voda R. s1192
Vohlidal J. s1088
Vohlídal J. s881
Voicu G. s1195
Vokal A. s928
Vokral I. s1132
Volant A. s924
Völkl J. s1193
Vollertsen J. s648
Vollmer D. s789
Vomiero A. s1172, s657
Von Tümpling W. s911
Von Wrochem F. s1424
Vopicka O. s1090
Vorkamp K. s1114
Vorotyntsev A. s935
Vorotyntsev I. s818
Vorotyntsev V. s1260
Vos J. G. s944
Vostalova J. s1117
Vostracka T. s1154
Vranckx S. s815
Vrchotova N. s1170
Vrkoslav V. s1130
Vrublevska T. s1114
Vukotic V. N. s729
Vuluga D. M. s1034, s1034
Vyklicky L. Jr. s1301, s778
Vyklicky V. s1301, s778
Vyskocil V. s1135, s1146, s1156, s597
Vytrasova J. s1162

W
Wächtler M. s699, s830, s862
Wacker L. s637
Wadhwa K. s1425
Wagner B. s1098
Wagner N. L. s812
Wagner T. s1206
Wakasugi A. s1238
Walczak B. s614, s614
Wales D. s1245
Wallner G. s923
Walshe A. s924
Waltar A. E. s638
Walter N. G. s872
Walter S. s1030, s1099

Walter S. M. s1040
Walther M. s686, s709, s881, s883
Wandlowski T. s1078
Wang D. s1104
Wang H. s1099
Wang W. s1103
Wang X. s810
Wangler T. s648
Warakulwit C. s595
Warchol J. s1425
Ward M. D. s834
Ward T. s756
Wardle N. s943
Waser J. s1100
Waser M. s1020, s1024, s758
Wasielewski M. s828
Wassermann B. s830, s877
Wasserscheid P. s810
Watters D. s790
Weber E. s1019
Wedzicha B. s671, s676
Wegener J. s800
Wegner H. A. s755
Wei Z. s1237
Weigand J. J. s946, s947, s960, s965, s1070, s773
Weiher F. s711
Weiner S. s832
Weingart H. s887
Weinstein J. A. s996
Weis M. s1019
Welther A. s1100
Wende R. C. s853
Wende W. s902
Wenge A. M. s808
Wennemers H. s776
Wentzell P. s613
Wenz G. s1296, s1320, s1321
Werner I. s1363
Westerlind U. s775
Westermann B. s1275
Wet R. s1178
Whiddon Francillard B. s624
White N. G. s863
Whittell G. s954
Whittingham W. s1101
Wickleder C. s952
Wickleder M. s932
Widyaya V. T. s1182
Wielens B. s613
Wild A. s1102
Willner I. s737
Wills M. s758
Wilsdorf M. s1364
Wimmer L. s718
Wimmer Z. s1006, s1086, s1089, s1101, s1307, s1321
Wimmerova M. s1307
Winkler K. s1260
Winn C. s1101
Winter A. s1102, s1102, s781, s973
Winterhalter M. s887
Wintner J. s1265
Wirsing A. s877
Wirtz M. s882
Wirz J. s1265
Witt A. s698, s951
Woell C. s838
Wohlrab S. s663
Wohnig S. s1364
Wojciechowski T. s1260
Wollgarten M. s1256
Wolun-Cholewa M. s1425
Wolska M. s690
Won S. s1164
Wong A. s608
Wong Y. C. s1162
Wong Y. S. s714, s803
Worrall J. s884
Worsfold P. s603
Worsley M. s1205
Wright A. s846
Wu P. s814
Wu S. s814
Wu Y. T. s806
Wuensch C. s705
Wunderlich N. s1193
Würtele C. s977
Würth C. s612, s903
Wuthrich K. s590
Wuttke E. s1156

X
Xiang Y. s933, s942, s993
Xiao C. s840
Xie L. s1103, s1103
Xu G. s1104

Y
Yagci Y. s788
Yakimova M. s1157
Yaku H. s899
Yalcin S. s919
Yamaguchi J. s759
Yamahata A. s1208
Yamamoto H. s853
Yamane I. s1232
Yamazaki T. s893
Yammine P. s1104
Yang S. s1261
Yankova A. s901
Yanovych D. s1171
Yardeni G. s1241, s952
Yarimkaya Bas S. s1128
Yaroslavtsev A. s1171, s1219
Yasar O. s1193
Yasmeen F. s725
Yasser O. s1264
Yasuoka K. s818
Yates P. s634
Yeasmin Z. s1244
Yefet M. s797
Yi H. s790
Yi L. s1187
Yildiz G. s1142
Yilmaz N. s1149, s610
Yim C. s1052
Yim J. H. s1105, s1310
Ying J. Y. s654
Yogendra S. s773
Yoon S. K. s1052
Yoon W. Y. s655
Yoon Y. s1173, s1176

Yoshinaga K. s1365
Youssef A. s994
Youssef N. s982
Yu B. Y. s655
Yu H. s1261, s1262, s1319
Yuan H. s720
Yuce N. s1153
Yun H. S. s926
Yun K. H. s1039
Yun S. s937, s972
Yusop R. M. s1307
Yuzhakova T. s1188, s643

Z
Zaarour L. s1262
Zabarska N. s943
Zabel A. s973
Zabrocka L. s1425
Zaccheroni N. s749
Zacchini S. s680, s681
Zacharovova K. s1365
Zadny J. s1121
Zadok A. s1258
Zagami R. s1216
Zagorac D. s851
Zagvozdkina T. s1134, s1157
Zahl A. s939, s958
Zahn D. s826, s881, s990
Zahn D. R. T. s1221
Zahoor M. s915, s915
Zaitsev V. s901, s902
Zakharova L. s1042
Zakharova M. s942
Zalesak B. s895
Zalewska K. s665
Zalewski P. s895
Zamalyutin V. s991
Zampese J. A. s996
Zamyatina A. s1299, s854
Zanni T. s1157
Zanotti V. s681
Zaouris D. K. s808
Zapf A. s637
Zarra S. s733
Zatloukalova M. s1158
Zavadilova A. s922
Zavazalova J. s1158
Zaverkina M. s1105, s1366
Zavoianu R. s1186
Zboril R. s1219
Zednik J. s1088
Zedník J. s881
Zeitler E. L. s693
Zeitler K. s1031
Zelenka T. s1366
Zemanek G. s897
Zemtsov L. s1219, s1232
Zengin E. s1022
Zenneck U. s695
Zevenhoven R. s692
Zewail M. s1106
Zeytuni E. s1106, s1107
Zgazar M. s1090
Zhabinskii V. s1107, s856
Zhang B. s1262
Zhang H. s650
Zhang J. s1228
Zhang W. s792
Zhang X. s610, s792
Zhang Y. s830
Zhao S. s1103, s1103
Zhdanova A. s902
Zhivotova E. s882
Zhu B. s1319
Zhu K. s729
Zhurov K. s602
Zhylitskaya H. s1367
Zidki T. s1241
Ziereis K. s1089
Zigah D. s595, s744
Ziganshina E. s597
Zilbermann I. s1241, s952, s958
Zilm K. W. s812
Zima J. s1117, s1139, s1158
Zimcik P. s1279
Zimmermann T. s1108
Zinchenko A. s882
Zindler M. s1026
Zitterbart R. s1367
Zivanovic V. s645
Ziyatdinova G. s597
Znaleziona J. s1117, s1144
Zobrist J. s644
Zoric D. s1188, s1194
Zrineh A. s909
Zucek K. s1130
Zuilhof H. s783
Zuravka I. s902
Zvatora P. s1159

[2,3-a]Pyridine Benzamide s883
[3+2] Cycloaddiotn reaction s1016
[60]fullerene s1079
[60]fullerene, [4+2] monoadducts s1057
§-Thalassemia Patients s1123
1,2-addition s763
1,2-phthaldehyde s1336
1,3,4-oxadiazole s1336
1,3-benzoxazin-4-one s1340
1,3-dipolar cycloaddition s1309, s1367
1,4-addition s962
1H-NMR s1166
1H-RMN s1160
2-Acetylthiophene s1347
2-amino-4H-chromene s1061
2-aryltetrahydrofurans s1023
2-hydroxymethyl-oxazolidinones s692
2-oxazolines s1034
3,4-di(methylene)tetrahydrothiophene-1,1-dioxide s1057
3-aminoquinoline-2,4-diones s1342
3D-QSAR s900
3-hydroxyquinoline-2,4-diones s1342
4-methylimidazole s1165
4-methylpentan-2-one s1177
5-amino salicylic acid s1254
5-aminopyrimidines s1077
7-hydroxycumarine s1061
A3-coupling s784
Ab initio s845
ab initio 6-31G method s867
Ab initio calculations s654, s808, s815, s818, s819, s860, s862, s863, s871, s872, s873, s874, s876, s879, s1130, s1226, s1242
ab initio energy landscape s1200
abcg2 s884
Abramov-type phosphonylation s1277
Absorption s640, s689
absorption correction s865
acid drainage s925
Acid mine drainage s640, s642, s926
acid mine drainage (AMD) s924
acid-base dissociation constants s1121
Acidity s642, s645, s782, s1148
Acridone s900
acrylates s868
acryloyl chloride s1069
actinide s639
Actinides s638
activated sludge s693
Activation s679
Activation energy s816
active lone pairs s1200
actuator s1247
Acyclic N-nucleosides s1347
a-cyclodextrin s610
Acylation s780, s853, s1004, s1036, s1042
acylhydrazone s1332
adhesion s655
adsorption s641, s647, s666, s705, s737, s793, s814, s842, s873, s1062, s1199, s1231, s1335
Adsorption of As(III) s915
Adsorption of humic acid s915
Adsorption studies s908, s908
adulteration s673
aggregation s721, s889, s986, s1033, s1216, s1219, s1252, s1278, s1319, s1335
agostic interactions s871
a-Iminocarboxamide-Nickel(II) Catalyst s1327
air pollution s910
Alcohols s653, s670, s683, s707, s758, s806, s1226, s1276, s1283
Aldehydes s1070, s1103, s1276, s1289, s1293
Aldol reaction s1084, s1264, s1269, s1363
algae s1178
Alkalinity s1138
Alkaloids s759, s804, s930, s1100, s1180, s1291, s1325, s1361
Alkanes s591, s683, s864
alkenes s684, s1050, s1071, s1082
alkyl isocyanides s1061
alkyl/aryl pyrenyl sulfoxides s1349
Alkylation s831, s894, s1011, s1020, s1057
Alkyne s806
Alkynes s684, s1011, s1066, s1078, s1098, s1218, s1328
Allenes s1052
Allosteric indicator displacement assay s861
Allosterism s1243
alloys s1251, s1252
allylation s1059, s1074
allylsilane addition s1284
alternative solvents s1182
Aluminium s661, s1163
Aluminum s1105, s1201
Alzheimer's disease s896
Amalgams s597, s1135, s1146
Amberlyst-15 s1023
amides s773, s1006, s1050, s1052, s1070, s1089, s1101, s1306
amination s761, s769, s801, s802, s1042
amine ligands s997
amines s689, s1006, s1050, s1289, s1293
amino acid s606, s899
Amino acids s651, s665, s720, s765, s791, s833, s879, s942, s1009, s1020, s1046, s1060, s1069, s1084, s1106, s1168, s1318, s1333, s1338, s1345, s1363
Amino alcohols s767
amino silane s1176
aminoacids s1269
Aminoalkylphosphonic acids s1046
aminobisphenol s962
Aminocarbonylation s1333
ammonia s818
Ammonia synthesis s808
Amorphous materials s832, s965, s1206
Amperometric detection s1139
Amperometric gas sensor s1134
Amperometry s1117
amphiphiles s787, s789, s790, s1025, s1169, s1317
amphiphilic block copolymer s792
AMP-PAN s635
Amyloid beta-peptides s710, s889

amyloid-§ peptide s896
analgesic agent s1274
analysis s899, s922
analysis of variance s614
Analytical chemistry s1146, s1152
analytical method s1083, s1257
Analytical methods s596, s599, s600, s604, s611, s612, s613, s614, s616, s637, s662, s673, s859, s917, s1036, s1055, s1102, s1114, s1124, s1128, s1135, s1138, s1141, s1145, s1148, s1154, s1154, s1156, s1160, s1161
Analytical Techniques s1123
Anayltical method s1168
Angiogenesis s898
anhydrides s1311
Anion recognition s863, s1324
anions s800, s835, s932, s953, s1035, s1155, s1159, s1222, s1290, s1296, s1331
Annulation s804, s1100
Annulenes s1322
Anodic oxidation s647, s906, s916
anthelmintic drug s1132
anthranilic acid s1340
Anthropogenic s918
Antibiotics s676, s684, s716, s719, s722, s895, s983, s1064, s1090, s1171, s1318, s1364
Antibodies s602, s1129
anti-cancer agents s1079
antidepressant s648
antiferromagnetic interaction s934
antifungal agents s950, s1101
Anti-impotence drugs s1164
Antimicrobial s1265
antimicrobial peptides s886
Anti-miR s709
antimony s924, s950
Antioxidant s674, s897, s899, s1125
antioxidant activity s1119, s1161
antioxidants s597, s678, s722, s901, s901, s1077, s1086, s1161, s1169, s1180, s1307
Antiproliferation s721, s1170
antiproliferative activity s982
antiprotozoal s1059
Antiprotozoal agents s714
anti-tubercular activity s874
antitumor s1254
Antitumor activity s1347
Antitumor agents s713, s896, s902, s957, s1020, s1101, s1220
antiviral activity s1294
antiviral agents s787, s1042, s1141
AOP s688
Apocarbonic anhydrase s914
apparent molar volumes s825
Appel reaction s1365
aprotic solvents s1065
Aptasensor s1127
Aquatic environment s904
Aqueous s1280
aqueous normal phase LC s1151
Aqueous solution s914
areal repeat units s747
Arenes s765, s774, s1014, s1285
Aromatic Chemistry s858
Aromatic substitution s1043, s1349
Aromaticity s819, s871, s1169, s1322
aromatics s747
arsenic s641, s912, s1152
Artesunic acid s1079
Artificial metalloenzymes s756
artificial photosynthesis s988
Aryl azides s1309
arylaminooxazoles s898
arylation s1084, s1314, s1337
arylguanines s1314
Aryl-Chlorides s1022
aryne chemistry s1015
Arynes s1314
ascorbate s884
Aspartame s1343
Association constant s867
asymmetric allylic alkylation s762
Asymmetric amplification s817
asymmetric catalysis s589, s665, s700, s707, s754, s758, s758, s759, s762, s763, s778, s779, s783, s1012, s1020, s1087, s1094, s1258, s1273, s1289, s1317
asymmetric cyclopropanation s1074
asymmetric hydrogenation s762
Asymmetric reaction s1277
asymmetric reduction s1094
Asymmetric synthesis s703, s707, s754, s774, s855, s956, s1024, s1044, s1071, s1088, s1100, s1264, s1273, s1277, s1278, s1282, s1286, s1287, s1308, s1363
Atmospheric chemistry s637, s863
Atom transfer radical polymerization s1104
atomic absorption spectrometry s1147
atomic alloys s593
atomic force microscopy s849
Atomic force microscopy (AFM) s1215
atomic metals s593
atom-transfer radical addition s1074
ATR FT-IR s639
Atropisomerism s1002, s1055, s1055, s1244
attenuated total reflexion s613
Aurophilicity s860
Autocatalysis s737, s780, s817, s1024
Autoxidation s1007
auxin s1101
Avrami Equation s1344
axial chirality s1325, s1348
aza-bisoxazoline ligands s1074
azahelicenes s1121
Azasugars s1023
azetidines s1313
Azide s1280
Azides s1002, s1011, s1043, s1297, s1299
aziridinyl phosphonates s1284
Azo compounds s654, s780, s798, s1040, s1041, s1114, s1211, s1266, s1272, s1355, s1358

azobenzene s734, s738, s1028, s1034, s1034
azomethine s1061
azomethine ylides s1267
Baby Foods s1140
Bacteria-modified red mud s908
Bacteria-modified silica fume s908
bactericidal activity s1126
bacteriorhodopsin s604
barite s1138
Barium aluminoborate glass s1253
Barrier properties s1072
base s1092
base materials s1186
basicity s643
BDD electrode s647
Bentonite s919
benzene s872
Benzenesulfonamides s890
benzobarrelene s962
Benzofuroxan s1149
Benzoxanthene s1022
Beta-Cell s723
beta-hydroxamides s1094
betalain s674, s861
betuline s818
Biaryls s1022, s1055, s1055, s1080, s1348
Bibenzimidazole s1352
bile acid s1066
bile acids, mixed micelle, Tween s875
bimodal imaging s735
binaphthyl derivatives s798
Binary mixtures s867
Binding constant s890
binfuctional catalysis s1013
Binol s1198
bioaccumulation s648
Bioaccumulationfactor s911
bioactive molecules s766
Biocatalysis s703, s705, s706, s707, s707, s708, s778, s802, s1292, s1342
biocide leaching s648
Bioconjugate chemistry s1297
Biodegradation s904
biodiesel s659, s926
bio-fixation s690
biofuels s1178
biogenic amines s677
biogeochemistry s603
biogeometallury s640
biochar s925
Bioinformatics s613
Bioinorganic chemistry s684, s685, s686, s756, s810, s819, s832, s983, s1185
biological activity s642, s684, s724, s740, s788, s793, s897, s901, s1000, s1025, s1049, s1071, s1108, s1159, s1170, s1180, s1251, s1257, s1287
biomarker c-erbB-3 s1150
Biomass s653, s675, s970, s1091, s1178, s1180
biomass burning s916
Biomaterial s710
Biomemetics s997
Biomimetic synthesis s703, s810, s1292
biomolecules s807
Bioorganic chemistry s721, s796, s892, s1069, s1082, s1164, s1330, s1367
Biophysics s885, s891
Biopolymer s1215
biopolymers s1303
bio-polymers s728
Biorefining s675
Biosensor s606, s608, s1150
biosensors s595, s608, s609, s687, s792, s876, s1120, s1123, s1129, s1146, s1221
biosorption s919
biosynthesis s703, s1292, s1318
biotechnology s712
Biotin-avidin technology s756
Biotransformations s652, s705, s892
bipolar electrochemistry s744
Bismuth s881, s950, s1156
bismuth nanoparticles s1256
bismuth oxide s990
bismuth oxido cluster s990
Block Copolymers s787, s789, s792, s793, s796, s834, s1038, s1291, s1303, s1341
block co-polymers s954
blocking layer s1172
blood substitutes s888
Blue phophorescent s937
Bodipy s1320
Bolaamphiphiles s1229
Bond energy s859
bond theory s820, s871
book s620
borane s1329
borane reduction s1094
Boranes s942, s1071
Borates s1050, s1080, s1112, s1285
Boron s805, s1036, s1050, s1111, s1177, s1286, s1295
Boron-doped diamond anode s916
borylation s1281
Bovine Serum Alb_min (BSA) s1113, s1113
bowl-shaped molecules s1056
Br?nsted acid-base s1317
Brassinolide s1107
Brassinosteroids s856, s1107, s1367
brazilian program s1175
Breast cancer s604, s1150
breast cancer resistance protein s884
Bridging ligands s679, s953, s985
Bromhexine s1139
bromine s1321
Bruker s1125
buffer layer s1222
Bulk heterojunction solar cells s790
Cadmium s645, s912, s1109, s1137
Cadmium removal s908, s908
Cadmium telluride s1236
caesium-137 s920
Cage compounds s695, s799, s820, s823, s844, s946, s961, s1245
calcite s642
calcium s692
Calculated water exchange reactions s883
calix[4]arene s1069, s1299

calix[4]arenes s1301, s1352
calixarene s1019, s1288
Calixarenes s767, s794, s1281, s1354
Calixarenes, polymers, macrocycles s770
Calorimetry s786, s1204, s1204
cancer s590, s713, s720, s892, s1029, s1102, s1148, s1154, s1233, s1279
Cancer cell line s883
Candida albicans s1332
Capability of detection s1141
Capillary s1165
capillary electrophoresis s1144
capsaicin s1131
capture s1176
Caramel s1165
carbanion s989
Carbanions s695, s768, s968, s1280
carbazole s1311
carbendazim, BAM s648
Carbene s682, s968, s972
Carbene homologues s702
Carbene ligands s694, s695, s696, s938, s959, s960, s967, s968, s1216, s1270, s1354
Carbenes s694, s760, s945
carbenoid s989
carbenoids s695
Carbides s680, s970
Carbocations s1099, s1345
carbohydrate s872, s1029
Carbohydrates s601, s740, s783, s854, s977, s1063, s1084, s1118, s1122, s1299, s1364
Carbon s637, s740, s1216
Carbon aerogel s1366
Carbon Allotropes s803
Carbon ceramic electrode s1137
Carbon dioxide s690, s690, s1111, s1112, s1176
carbon dioxide capture s1177
Carbon dioxide fixation s661, s662, s665, s689, s691, s842, s1174, s1193, s1300
carbon material s1192
carbon nanotube s741
carbon nanotubes s739, s744, s1247
carbonation s692
carbonyl s981
carbonyl compounds s1059
Carbonyl ligands s680, s938
Carbonylation s694, s756, s1191, s1300
carboranes s942, s1006
carborate anion s764
Carboxamide dimers s1333
carboxylate s981, s984
Carboxylate ligands s696
carboxylation s665, s683, s705
carboxylic acid s825
carboxylic acids s705, s765, s979, s1000, s1050
cardiovascular diseases s1117
career days s669
Carotenoids s1161
CARS (Coherent Anti-Stokes Raman Scattering) s606
cascade s1267
cascade reaction s802
catalase s907
Catalysis s678, s683, s701, s760, s761, s856, s950, s962, s962, s981, s987, s1095, s1098, s1100, s1295, s1336
Catalyst s654, s796, s1022, s1105, s1219, s1248
Catalyst Reuseability s1185
catalyst support s655
catalysts s592
catalytic reduction s935
Catechol oxidases s997
catecholamines s812
Catenanes s737
Cation s960
Cations s591, s787, s946, s965, s1096
caustic magnesia s642
Cavitands s794, s797, s1058, s1242
CBS-4M s1142, s1149
C-C activation s765, s1273, s1312
C-C bond formation s1046
C-C coupling s761, s766, s774, s1001, s1002, s1067, s1088, s1218, s1285, s1285, s1302, s1317, s1326
CD spectroscopy s893
C-debenzylation s1342
Cell Adhesion s726, s783, s1028
cell culture media s1116
cell delivery s1307
cell migration/invasion inhibitor s1319
cellular uptake s1238
Cellulose - based carbon aerogels s1189
cellulose acetate s818
Cellulose-based polymer s1215
Ceramics s970, s1188, s1194, s1203
Cerium s663
cesium s635
C-F activation s1266
C-Glycosides s1354
C-H activation s591, s694, s696, s716, s759, s759, s769, s819, s823, s951, s1014, s1018, s1042, s1051, s1082, s1281, s1285, s1349, s1357, s1361
C-H functionalization s1286
cinchona alkaloids s1338
cinnamadehyde hydrogenation s1197
cinnamaldehyde s1197
Circular dichroism s724, s864, s953, s1055, s1130, s1135, s1154, s1154, s1216, s1354, s1358
cis-trans isomerization s1034
civilization s619
clathrate s659
Clathrates s662, s691, s1174
Clay s1223
Clays s809
Clean synthesis s663, s1182
Cleavage reactions s872
click s1322

Click chemistry s658, s737, s784, s788, s797, s801, s842, s943, s998, s1002, s1011, s1035, s1035, s1049, s1056, s1068, s1086, s1243, s1275, s1281, s1282, s1296, s1297
cluster compound s939, s979
Cluster compounds s680, s694, s881, s942, s964, s1245
clusters s830
Co s993
C-O coupling s765
CO2 s692
CO2 and SO2 s847
CO2 capture s843
CO2 Capture, Amino Acids, Amine s1173
coagulation/flocculation s905
coal mine s925
Cobalt s944, s949, s951, s978, s987, s987, s990, s1213, s1300
Cobalt(II)-Glycine complex s1127
Co-crystal s1198
cocrystals s1235, s1249
Codoping s1175
COF s1079
Cofactors s1123
Collaboration s633
Collagen s711
Colloid s1365
Colloids s721, s1338
comb-copolymer s1104
Combinatorial chemistry s700, s1002, s1047, s1096, s1293, s1327
combinatorial synthesis s1028
combustion s912
Competency s927
Competing ions s651
compchem s623
Complexation s639, s1365
complexes s682, s980
Composition s1166
Computational Chemistry s591, s610, s811, s815, s819, s820, s830, s854, s878, s879, s1206, s1208, s1245, s1339
Computational methods s1343
Computational study s821
conbustion s916
condensation s682
conducting materials s789, s824, s1038, s1078, s1184, s1184, s1293, s1338
conducting polymer/platinum composites s1133, s1133
Configuration determination s1055
confinement s810
Conformation analysis s710, s978, s1091, s1102, s1130, s1204, s1343
conformation condition s1062
conformational effects s807
Congo red s897
conjugate addition s1041
conjugated oligomers s1083
Conjugated polymers s790
Conjugation s766, s1040, s1057, s1085, s1101, s1345
contaminated biomass s912
Contaminated municipal waste s636
contamination s646
continuous flow chemistry s664
continuum cluster s859
controlled-radical polymerization s792
Cooperative effects s1187
cooperativity s1013
coordination s747
coordination compounds s940
coordination frameworks s969
coordination chemistry s939
Coordination modes s948, s967, s977, s978, s983
Co-phthalocyanine s910
Copolymerization s1066, s1102, s1335
co-polymers s888
copper s612, s701, s709, s715, s717, s774, s889, s936, s954, s955, s975, s977, s996, s1065, s1074, s1087, s1111, s1155, s1223, s1232, s1243, s1273, s1349
copper catalysis s763
copper catalyst s784
Copper Complexes s941
Copper removal s914
copper, cobalt s1197
copper-picolinate s1203
Coprecipitation s903
corannulene s1281
core-shell nanoparticles s1261
Cork s651
Corrosion s1118
Coumarin s1265
Coumarin 120 s1115
Coumarin 35 (C35) s1113, s1113
coupling agent s1090
coupling reactions s766
CPD/DCPD s1182
cracking s654
cross - linking s1189
cross coupling s941, s1086
Cross Dehydrogenative Coupling s1310
Cross-bridged cyclen s941
Cross-coupling s696, s701, s719, s736, s754, s759, s760, s761, s772, s801, s960, s975, s1014, s1022, s1042, s1045, s1054, s1070, s1097, s1273, s1286, s1297, s1322, s1328, s1357, s1361
Cross-Couplings s856, s1230
crown ethers s734
Crystal engineering s799, s834, s837, s844, s847, s1174, s1346
Crystal enginnering s659
Crystal growth s659, s786, s810, s835, s837, s850, s850, s1174, s1204, s1307
Crystal structure s997
crystallization s1039, s1205, s1260
Crystallization behaviors s1248
crystallographic computing s865
C-S, C-Se, C-P bond forming reactions s975
CT complex s1265
Cu s1183
Cu(II) complexes s935
Cupper(II)-Glycine complex s1126

Cuprates s973
CVT s850
cyanides s837, s982, s1289
cyanido complexes s934
cyanobacterial hepatotoxins s598
cyanoethylation s1092
Cyanosilylation s1337
Cyclability s959
Cyclen s941
cyclic esters s1311
cyclic voltammetry s649, s890, s924, s996, s1126, s1128, s1424
Cyclisation s661, s1180
Cyclization s1002, s1007, s1012, s1024, s1029, s1042, s1052, s1057, s1086, s1098, s1100, s1103, s1271, s1283, s1298, s1305
Cycloaddition s695, s714, s755, s791, s845, s1066, s1088, s1314, s1333, s1337, s1346
cycloadditions s823, s865
cyclodehydration s1340
Cyclodextrin s735, s833, s1320
Cyclodextrin complexes s1343
Cyclodextrins s768, s827, s1021, s1204
Cyclohexene oxidation s987
cycloisomerization s757, s1263
Cyclooligomerization s1324
Cyclopentadienyl ligands s755, s1363
cyclopropylphosphonates s1287
cyclovoltammetry s1156
cytochrome b5, s866
cytochrome c s884, s1215
cytochrome p450 s866
Cytochromes s727
cytotoxicity s791, s883, s892, s949, s954, s991, s1006, s1181, s1315
Danube s917
data fusion s615
DBP, BBP, DEHP s1163
dearomatization s1059
Decarboxylation s1180, s1269, s1338
decontamination s929
Deemulgation s1062
Defects s816
degradation s693
dehalogenation s760
Dehydrogenation s1326
dendrimer s1323, s1334
Dendrimers s720, s731, s755, s787, s790, s938, s1053, s1214, s1262, s1336, s1362, s1425
dendronized polymers s1262, s1323
density s825
Density functional calculations s591, s689, s771, s781, s788, s814, s820, s822, s823, s823, s824, s865, s868, s872, s880, s967, s971, s1075, s1208, s1351
Density functional theory s813, s824, s990
densiy s1253
depolymerization s1320
deposition s1221
deracemisation s759
Determination s1123, s1140, s1140
devices s1061
DFT s861, s1149
DFT calculations s610, s963
DI s1131
Diabetes s723
diacetylene s1287
diamino-benzodifuran s1061
diastereoselective synthesis s1059
Diastereoselectivity s991, s1031, s1274, s1298, s1358
diazaanthracene s1320
diazenyl s1069
Diazo compounds s595, s774, s1009, s1018, s1317, s1358
diazoacetates s1074
diazonium salts s1084
Diels-Alder reaction s1233
diene s962
diesel component s1177
Diethanolamines s950
Differential pulse voltammetry s608, s1139
diffusion coefficient s1144
dihydrocapsaicin s1131
diiron complexes s681
dilactams s1075
dilatation coefficient s1253
dilatometric curves s1253
Dimerization s1033
Dimethyl Carbonate s661
dimethyl phthalate s910
dioxin s906
direct synthesis s1179
disinfectant s1126
disperse alkaline substrate s642
dissociation energies s610
Dissolved Organic Matter s650
distillation s1260
divergence entropy s877
DMSO oxidation s1077
DNA s711, s712, s731, s737, s796, s811, s862, s879, s890, s891, s899, s954, s969
DNA adducts s1314
DNA cleavage s724, s902, s1039
DNA damage s713, s1011
DNA interaction s598
DNA methylation s1082
DNA Nanotechnology s834
DNA recognition s1011
DNA Structures s730
Docking s900
Domino reaction s803
Domino reactions s765, s804, s1298, s1305, s1316
Donor acceptor systems s805
donor-acceptor s1033
Donor-Acceptor pairs s1212
Donor-acceptor systems s741, s1218, s1293, s1324, s1360
Dopamines s1243
Doping s1196
Double Logarithmic Plot s1113
doxorubicin s1238
drilling mud s1138
Drinking Water s1140
drug s601
Drug delivery s730, s750, s796, s946, s1025, s1148, s1204, s1228, s1233, s1244

Drug design s719, s778, s898, s1000, s1141, s1306, s1307, s1323, s1332, s1343
Drug discovery s718, s721, s894, s898, s901, s1005, s1056, s1090
drug load s1238
drug screening s712
Drug-delivery s796
dye loading kinetics s1172
dye sensitized solar cells s1172
Dyes/Pigments s893, s930, s1123, s1143, s1345
Dye-sensitized solar cell s1172
Dye-surfactant interaction s1112
dynamic covalent chemistry s1044
dynamic kinetic resolution s1274
ECD s1357
education s619, s633, s928
Efficiency of impregnation s1147
Elastomers s1282
e-learning s624, s928, s929
elecroanalysis s598
Electrical conductivity s867
electrical double layer s1138
electride s870
electroanalysis s598
Electroanalytical chemistry s1126, s1127
Electrocoagulation s647
Electrochemical glucose detection s609
Electrochemical impedance spectroscopy s1150, s1150 s1424
Electrochemical oxidation s1110
Electrochemical sensing s1127
Electrochemical simulation s1127
Electrochemistry s593, s594, s595, s595, s596, s597, s666, s788, s825, s947, s958, s1001, s1003, s1109, s1128, s1135, s1137, s1143, s1146, s1156, s1158, s1173, s1180, s1184, s1184, s1217, s1242, s1247, s1296
Elechromic s1425
Electron diffraction s848, s850
electron exchange columns s958
electron microscopy s1038, s1188
Electron spin resonance s1167
Electron transfer s590, s681, s739, s741, s828, s880, s988, s1128, s1250, s1255, s1305, s1324, s1360
electron transport s740, s1078, s1184, s1184, s1360
electron-deficient compounds s1341
electronic structure s814, s820, s824, s860, s871
Electronic Transport s824
electro-oxidative lithography s849
Electrophilic substitution s769
electrophoresis s604, s768, s1136, s1136, s1157
Electroplating s1205
Electrorheological Fluid s1223
Electrospray ionization s1155
electrostatic interaction s868
ELF s820
Elimination s610
ELISA method s1162
emission s1033
Enaminone s1294
enantiomer separations s602
enantioselective catalysis s756
enantioselective synthesis s1313
Enantioselectivity s604, s703, s706, s714, s769, s817, s963, s1004, s1025, s1045, s1055, s1078, s1085, s1091, s1091, s1094, s1316, s1358, s1361
enantioseparation s753
Enediynes s771
energy s1175
Energy Conversion s653, s701, s1178, s1179, s1184, s1184, s1185, s1255
energy dissipation s604
energy landscape s851
energy relationships s1115
Energy transfer s659, s738, s746, s815, s938, s1214, s1360
enolethers s1092
enteromorpha linza s919
Environment s650, s906
Environmental Ethics s631
Environmental chemistry s602, s635, s637, s638, s641, s642, s643, s645, s646, s649, s652, s656, s725, s863, s909, s913, s913, s1008, s1137, s1152, s1158, s1179, s1189
environmental sample s921
environmental stress s907, s918
Enzymatic CO2 reduction s693
enzymatic polymerization s1303
enzyme s606, s715
enzyme catalysis s611, s706, s708, s872, s894, s898, s1190, s1321
Enzyme design s756
enzyme models s685, s704, s892
Enzymes s589, s712, s816, s954, s1004, s1068, s1118, s1136, s1332
Epibrassinolide s1107
Epitaxy s1209
epithermal neutron activation analysis s910
Epoxidation s803, s963, s978, s1085
EPR spectroscopy s1169, s1241
equilibrium constant s868
equilibrium study s886
ergosterol s1332
Escherichia coli s1148
ESR s880
esterification s659
ethanol s1219
Ethics s619, s930
ethics - transdisciplinary education - -scientific and enterprise responsibility s628
Ethics of science s630
ethylene s612
Euclidean distance s614
evaluation s634
evolved gas analysis s1344
EXAFS spectroscopy s1220
excited state s821
excited-state dynamics s781
Exchange interactions s970, s1037, s1293
exons s877
Experimental design s616

explicit solvent s859
extraction s929, s1149
extraction by ultrasonic probe s1124
eycn s669
facade coating s648
Factor detection s615
False compliance s1141
fatty acid biosynthesis s719
Fatty acids s653, s1268
fault detetection s617
FeCrAl s655
feedback s634
Femtochemistry s827
fermentation s613
fermented food s677
ferrocene s1043, s1316
Ferrocene-modified silica nanoparticle s1127
ferrocenyl diphosphine s763
ferromagnetic interaction s934
fibers s601
fire extinguishing substances s809
Fischer carbene complex s980
flame radicals s809
Flavin s1087
flavonoid s674
flavour formation s672
flow s1254
flow cytometry s1332
flow chemistry s663
flow injection s603
Flow injection analysis s1139
flow systems s596
Flue gas purification s664
fluoprescence s1086
Fluorescence s605, s687, s699, s711, s748, s781, s802, s838, s1011, s1031, s1049, s1088, s1111, s1115, s1120, s1224, s1226, s1279, s1297, s1320, s1321, s1349, s1362, s1364
Fluorescence anisotropy s1327
Fluorescence quenching s861
Fluorescence Resonance Energy Transfer Method (FRET) s1113
fluorescence sensor s1019
Fluorescence spectroscopy s611, s612, s784, s785, s891, s1113, s1113, s1122, s1226, s1270
fluorescence, fluorescent dyes s887
fluorescent nanoparticles s750
Fluorescent probes s590, s595, s611, s720, s784, s795, s882, s932, s1043, s1118, s1157, s1268, s1297, s1301, s1307
fluoresence s742
Fluoride s1324
fluorides s701
fluorinated s764, s979
Fluorinated ligands s755, s880
fluorination s1073
Fluorine s652, s801, s1016, s1050, s1051, s1052, s1091, s1285
Food s676
Food additive s1168
food analysis s617
food production s671
food quality s671
food safety s671
Food waste s675
formic acid s845
Franck-Condon factor s878
freely rotating chains s1032
Freshwater s650
Fret s1011, s1122, s1355
Friedel_Crafts s1266
fuel cells s1181, s1203
fuels s1175
Fukushima s635
fullerene s741, s1060
fullerenes s739, s799, s823, s865, s947, s1235, s1249, s1330, s1351
functional ligands s1093
functional thin films s744
Functionalisation s773
functionalization s961, s1281
functionalized adlayers s1095
fungicide s1162
Fusarium s1162
Fused-ring systems s772, s1031, s1326, s766
Future s619
gabapentin s890
Gadolinium s607
Ga-Ge-Sb-S s1206
Gallic Acid s647
gallium s757, s983
Gallium oxide s1227
Gallium sulfide s1227
gamma-alumina (?-Al2O3) s873
ganglioside s775
Gas chromatography s616, s1147, s1159, s1165, s1169, s1202, s1321
gas chromatography/mass spectrometry s725, s1124, s1167
gas phase s807
gas phase reactions s727
gas sensors s593
Gas storage s842, s847
gasoline adulteration s1175
gas-phase s869
Gas-phase chemistry s821
Gas-phase reactions s836, s1226, s1275
GC-MS s1160, s1166
GC-MS(EI-SIM) s1163
GCxGC-MS s618
GeF2 s1200
gel polymer electrolyte s1106, s1107
Gelation Time s1080
Gels s833, s1003, s1012
gentamycin s1116
geochemical archive s646
geomicrobiology s640
Germanium s1227
Glasses s663, s860, s882
Glassy carbon paste electrode s1139
global warming s1176
glycerol s1177
glycerol carbonate s692
Glycoconjugates s718, s740, s854, s1102
glycolipids s723
Glycopeptides s775
Glycoproteins s892

glycosylation s775, s822, s854
Gold s679, s752, s813, s942, s968, s984, s1007, s1052, s1073, s1098, s1098, s1216, s1220, s1254, s1262, s1263, s1270
gold nanoparticles s753
gold surface s1095, s1294
Gould-Jacobs reaction s770
G-quadruplexes s713
grafted particles s958
Grafting s1365
granite s923
grant proposals s667
Grape seed oil s1166
graphene s593, s739, s741, s741, s747, s809, s868, s876, s1058, s1184, s1237, s1246, s1271, s1333
Green chemistry s641, s652, s656, s656, s658, s660, s661, s662, s662, s665, s683, s696, s773, s783, s806, s856, s895, s1008, s1047, s1061, s1067, s1070, s1091, s1097, s1182, s1189, s1192, s1200, s1251, s1304, s1304
green marine algae s919
green materials s1193
Green Rust s903
greenhouse gas s1176
Grignard metathesis s1296
Grignard reaction s769, s1044
GST s851
halogen bonds s804
Halogen Dance Reaction s1300
Halogenation s1001, s1075, s1288, s1292, s1304, s1321
Halogens s1030, s1040, s1099
harmonic oscillator s878
H-bonded systems s604
HCN s873
health s906
Heat treatment s1205
heavy metal s919
Heavy metals s911, s912, s913
heavy-element chemistry s813
Heck reaction s941, s1001, s1018, s1045, s1361
Helical structures s740, s794, s838, s1001, s1010
Helium nanodroplets s1261
hemerythrin s888
hemoglobin s888
heparin s605
herbicide s1101, s1140
herbs s1119
Heterocycles s661, s718, s719, s754, s755, s764, s766, s766, s767, s772, s772, s777, s933, s973, s1002, s1004, s1005, s1009, s1037, s1042, s1052, s1054, s1064, s1066, s1074, s1075, s1090, s1098, s1098, s1275, s1283, s1285, s1296, s1312, s1313, s1353
heterocyclic s1340
heterogeneous catalysis s652, s658, s660, s663, s730, s752, s806, s824, s978, s1012, s1013, s1064, s1065, s1080, s1097, s1103, s1188, s1220, s1224, s1250, s1251, s1255, s1258
heterogeneous catalysts s692, s1191
heterogeneous catalytic oxdation s664
heterogeneous photocatalysis s1031
Heterogenous catalysis s663, s767, s1250
heterogenous catalysts s976
Heterometallic complexes s1016, s1093
Hetocycles s1096
Hexadecyltrimethylammonium bromide s647
Hexakis-adduct s1079
Hexamethylenetetramine s1080
hierarchically assembled ZnO s657
high hydrostatic pressure s677
high performance liquid chromatography s857
high pressure chemistry s839
Higher Amino Sugars s998
highlybranched polymers s1309
High-pressure chemistry s1111, s1112
high-purity substances s1260
high-troughput screening s897
histaminergic blockers s1018
histaminic receptor s1018
History s619, s620
History of chemistry s626
History of Science s621, s626, s627, s632, s931
homoallenyl azines s1359
homodimers s1079
Homogeneous catalysis s694, s696, s696, s701, s716, s755, s756, s757, s760, s765, s823, s944, s971, s992, s1014, s1023, s1042, s1047, s1051, s1054, s1066, s1082, s1098, s1185, s1191, s1285, s1291, s1302, s1361
Homogeneous cataylsis s1073
homogenous catalysis s769
homotaurine s811
honey s673
hormones s612
host cell protein s613
Host-guess systems s1208
host-guest s869
Host-guest complexes s1234
host-guest chemistry s1301
host-guest system s1275
Host-guest systems s733, s797, s837, s842, s1021, s1058, s1068, s1068, s1244
HPLC/UV/MS s1131
Huisgen cycloaddition s1300
human plasma s1116
Hybrid materials s1195, s1236
hybrid nanostructures s748
Hybrids s961
Hydrates s659, s662, s691, s1174
hydrazine s1331
Hydrazinobenzimidazole s1347
Hydrazones s896, s1096, s1275
Hydroamination s1306

Hydroaminoalkylation s1306
hydrocarbon s1276
hydrocarbon chemistry s1056
hydrocarbons s1130
Hydroformylation s1337
Hydroformylation/Strecker reaction s1333
hydrogel s1046
Hydrogels s1344
Hydrogen s949, s1178, s1245, s1354
Hydrogen bond s1033
hydrogen bonding s1287
Hydrogen bonds s700, s733, s734, s754, s767, s769, s794, s805, s814, s834, s863, s870, s882, s934, s1012, s1068, s1289
hydrogen bones s818
hydrogen peroxide s1179
hydrogen production s976
hydrogen separation s1177
Hydrogen transfer s771, s880
Hydrogenation s678, s700, s758, s761, s767, s779, s971, s1071, s1097, s1100, s1182, s1196, s1197, s1207, s1273, s1308
hydrogen-bond patterns s844
hydrochemistry s925
hydrophobic core s877
Hydrophobic effect s1037
Hydrophobic zeolite s849
hydrotalcites s1186
Hydrothermal s959
hydrothermal stability s1223
hydrothermal synthesis s953, s1209
hydroxamate based siderophores s886
hydroxamate complexes s886
Hydroxy phosphonate s1277
hyperbranched polyimide s1090
hyperbranched polymers s1309
Hyper-coordinated s960
hyperpolarizabilities s870
hyperpolarizability s986
Hypervalent compound s803
Hypervalent compounds s701, s1304
Hypervalent iodine s1059
chalcogenides s1206
Chalcogens s1196
charge transfer s748, s766, s828, s862, s1075, s1208, s1289
Cheese s677, s1141
Chelate s972
Chelates s715, s1363
Chelidonium majus s885
chemical durability s1253
chemical education s634
Chemical characterization s916
Chemical Speciation s650
Chemical vapor deposition s850, s1213, s1228
chemiluminescence s1279
chemiluminescence detection s606
Chemisorption s689
Chemistry s676, s930
Chemistry education s626
Chemistry Ethics s630
chemistry lecturer s633
chemistry proposals s667
chemoenzymatic s1274
Chemoinformatics s614, s619
chemometrics s615, s616, s617, s618, s673
chemoselective one-pot 1,4--elimination/[4+2] cycloaddition/aromatization s1057
Chemoselectivity s1054
Chemosensors s742, s1349
Chiral s1079
Chiral auxiliaries s1088, s1130
chiral dirhodium complex s1357
chiral imidate ligands s762
chiral ligands s1284
Chiral resolution s1055, s1056
chiral sulfoxide s1348
Chirality s665, s740, s753, s794, s794, s817, s838, s956, s1024, s1064, s1135, s1308, s1363
Chiroptical spectroscopy s1357
chiroptical switches s798
chitosan s1046, s1254
chloride s984
chloride poisoning s1133
chlorine s913, s1321
cholesterol s1086
Chromatography s602, s1351
Chromium s913, s1300
Chromium Triacetate s1080
chromogenetic substrate s1027
chromophore s1223, s1265
Chromophores s766, s812, s1031
Chronoamperometry s1127
Ibuprofen s906
ICP-AES s1134, s1157
identifying tracers in gasoline by GC/MS s1175
Illegal compounds s1164
Imaging agents s709, s717, s720, s749, s889, s933, s1136, s1228
imidazoquinoline s770
imine exchange s1044
Imines s1277
Immobilization s685, s705, s716, s1032
immobilization mechanism s1192
immunoassays s897, s1256, s1146
immunoglobulin s897
immunochemistry s609, s1221
Impact resistance s1248
Impregnation s959
Imprinting s1082
in vitro antiradical activity s935
Inclusion compounds s691, s818, s835
Indium s971, s1302
Indium mediated Allylation s998
indole s899, s1353
Industrial Chemistry s611, s627, s1063, s1103, s1111, s1112, s1339
industrial residues s1193
inelastic neutron scattering s847
Infant formula s1163
inflammation s897, s1000, s1246, s1267
infrared s810
Infrastructure s929
inhibitors s715, s722, s777, s894, s898, s1029, s1049, s1068, s1246, s1313, s1332

inkjet printing s712
inner-phase reactions s869
innovation s927
Inorganic Chemistry s667, s1253
Insertion s689, s690, s783
in-situ oxidation s989
Insulin s1106
intensive schools s624
intensive workshops s624
Intercalations s658, s1223
Interfaces s746, s797, s825, s1007, s1328
intergrowth s851
International Exchange s633
intramolecular cyclization s1359
intramolecular Diels-Alder s1319
Intramolecular Charge Transfer (ICT) s1115
Iodine s836, s1288, s1304, s1349
iodine(III) s1292
Ion exchange s651, s654, s966, s1176
Ion exchange resins s868
Ion channels s718, s1339
Ion chromatography s912
ion mobility s727
ion pair s1190
Ion pairs s651
Ion selective electrode s650
ion transport s804
ionic conduction s814
ionic conductivity s1106, s1107
ionic liquid s810
Ionic liquids s651, s662, s665, s841, s880, s899, s939, s945, s958, s973, s1032, s1036, s1116, s1128, s1181, s1193, s1200, s1216
ionization potentials s864
Ionophores s1281
IR s994, s1142
IR spectroscopy s606, s1165, s1351
iridium s694, s1083, s1312
Iridium Complexes s1028
iridium(III) complex s937, s972
Iron s678, s680, s683, s760, s761, s761, s819, s971, s974, s1100, s1123, s1213, s1234, s1290
Iron sulphide s808
iron(II) s980
Iron-Catalysis s1022
Irradiated foods s1167
IR-spectroscopy s818
Isomerizationss780, s1023, s1034, s1049, s1244, s1268, s1358
Isomers s859, s873
isoniazide s1137
isonicotinic acid s1065, s1334
isophthaloyl dichloride s1075
isothiocyanic acid s1342
Isotopes s638
Isotopic labeling s782, s1009, s1082, s1301, s1318
Isotopic labelling s637
ITO s849
ivermectin s1132
Jana2006 s865
Julia reaction s1050
Juvenile hormone binding protein s893
keggin s1203
ketal s1177
ketones s1045, s1052, s1103, s1276, s1289, s1304, s1357
key competences s624
Kinetic modelling s821
kinetic parameters s868
Kinetic resolution s611, s1004, s1094, s1190, s1258
Kinetics s611, s637, s649, s671, s683, s690, s733, s782, s811, s812, s815, s817, s831, s863, s944, s945, s949, s951, s1024, s1051, s1095, s1097, s1136, s1137, s1145, s1202, s1203, s1216, s1267, s1280, s1283, s1325, s1331
Kinetics Parameters s1344
kinetin s935
Lab-Automation s1327
Label-free s1127
Labeling s1107
laccase s674
laccase induction s885
Lactams s722, s777, s1315
Landfill leachate s647
Langmuir-Blodgett s1218
Langmuir-Blodgett films s809, s1255
languages for specific purposes s624
lanthanide complexes s1155
Lanthanides s731, s944, s1242
lanthanoids s989
laser ablation s1256
Laser spectroscopy s808, s826, s862
lateral substitution s1019
Late-transition metal s1310
layered compounds s658, s848, s1189
layered double hydroxides s1186
LC/MS s1164
LC/PDA s1164
lead s645, s813, s912, s913
lead sulfide s851
learning object s623
Lewis acids s755, s757, s854, s1103
Lewis adsorption sites s873
Li ion battery s959
Li Ion Diffusion s816
Li-batteries s995
library s775
ligand s962
Ligand coordination s980
Ligand design s720, s760, s782, s889, s957, s996, s1008, s1270, s1306, s1330
ligand effects s699, s949, s1267
ligands effects s696
Light s751
lignin s1191
Li-Ion Batteries s953
Linear free energy relationship s1280
Linear free energy relationships s1051
linear solvation s1115
LiNi1/3Mn1/3Co1/3O2 s995
lipid s926, s1025, s1117
lipid peroxidation s1077
Lipids s887, s1165, s1170
lipophilicity s778, s874

liposome s1232
liposomes s1006, s1129, s1318
liposomes, s887
Liquid Crystals s1033, s1282, s1330
liquid chromatography s599, s600, s726, s1120, s1124, s1128, s1136, s1138, s1139, s1140, s1148, s1151, s1153, s1158, s1162, s1167, s1168, s1169, s1171
Liquid paraffin s1168
lithiated sulfoxide s989
Lithiation s1355
lithium s695, s754, s957, s968
lithium battery s948
lithium nitride s814
Lithium titanium disulphide s816
Lithium vanadium fluoride s816
Lithogenous s918
lithography s1221
Living Ethics s629
L-lactide s1310
LLDPE film s1072
Logic gate s861
long-chain branch s1039
Lubricant s1105
Luminescence s731, s748, s749, s750, s785, s845, s862, s936, s943, s973, s996, s1192, s1195, s1196, s1200, s1206, s1211, s1214, s1323
luminescence properties s781
luminescent probe s1155
luminiscent s1223
Macrocapillary columns s1147
macrocycle s1075, s1083
Macrocycles s780, s799, s863, s887, s944, s956, s991, s1072, s1078, s1081, s1085, s1218, s1296, s1311, s1324, s1328, s1330, s1356
macrocyclic imide s1265
Macrocyclic ligands s941, s982, s1016, s1136, s1155
Magnesium s692, s754, s933, s1210, s1325
magnetic s910
magnetic materials s994
Magnetic Nanoparticles s1309
Magnetic properties s680, s698, s731, s749, s932, s934, s951, s974, s978, s982, s992, s992, s1036, s1228, s1234, s1240, s1250
magnetism s980, s1231
magnets s993
magnolol s1013
Maillard reaction s672
Main group elements s702, s873, s965, s1245
main group chemistry s688
Maingroup s960
MALDI matrices s1130
man s619
Manganese s678, s933, s946, s951, s984, s992, s1116, s1174, s1196
manganese and cobalt ions s886
manganese complexes s934
Mannich s1269
Mannich bases s765, s1024
marine environment s603
mass spectrometer s610
Mass spectrometry s596, s602, s613, s666, s723, s725, s726, s727, s727, s728, s728, s733, s827, s855, s892, s942, s1051, s1082, s1083, s1110, s1117, s1138, s1143, s1151, s1155, s1159, s1162, s1168, s1169, s1171, s1257, s1351
Mass spectroscopy s1170, s1281
Mass spectrum s1131
material science s1164, s1217, s1251, s1252
Materials Chemistry s858
Materials scienc s1033
Materials science s595, s643, s705, s726, s791, s809, s824, s832, s833, s834, s845, s846, s847, s1188, s1194
Matrix isolation s845
MCR-ALS s618
medical chemistry s670, s714
Medicinal application s856
Medicinal chemistry s705, s714, s718, s718, s719, s889, s1014, s1020, s1037, s1049, s1064, s1139, s1154, s1154, s1278, s1313
Medium-ring compounds s785
mechanical properties s1063, s1072
mechanism s683, s713
mechanisms s688
mechanisms of reaction s952
mechanochromic luminescence s969
membrane s608, s1248
membrane fusion s1232
Membrane proteins s727, s792, s812, s887
membrane reactor s1219
Membranes s885, s1129, s1170, s1181
Memory of chirality s771
mephedrone s1026
Mercury s646, s664, s913, s1138, s1152
mesoionic carbenes s700
Mesoporous s1227
Mesoporous film s609
Mesoporous materials s654, s682, s699, s730, s840, s841, s963, s1032, s1195, s1207, s1223, s1228
mesoporous molecular sieves s976
mesoporous silica nanoparticles s1013, s1212
metabolism s670, s1026, s1166
metabolites s601
metabolomics data analysis s615
metal alkoxides s993
metal alloy membrane s1177
Metal and metalloid contamination s644
metal bioavailability s925
metal catalyzed asymmetric synthesis s1284
metal catalyzed reactions s656
metal complex s738, s1027
metal complexes s1093, s1125, s1318
metal foam s655
metal nanoparticles s748
Metal Organic framewords s1287
metal organic framework materials s847
metal phosphonate s1362

metal supported catalysts s1197, s1197
Metalation s1274, s1350
metallaboranes s990
Metallacycles s859, s985
Metallic glass s1205
metallocenes s855
Metalloenzymes s706, s771
Metallomesogens s680
metal-organic frameworks s729, s782, s785, s838, s841, s936, s1030, s1202, s1207, s1258, s1326, s1345
Metals s651, s1207
metastable phases s990
Metathesis s592, s882, s1009, s1010, s1023, s1032, s1076, s1095, s1096, s1182, s1190, s1268, s1291, s1316
methanol oxidation s1181
Methicillin-resistant Staphylococcus aureus (MRSA) s890
Methyl Radicals s1241
Meyer-Schuster rearrangement s1073
micelles s827, s1035, s1268, s1290, s1355
Micelles,Molecular recognition s875
Microalgae s926
microAnalyzer s1148
microarrays s712
microbial water quality monitoring s1148
Microcystin-LR s598
microelectrode s598
Micromotors s744
Micropore materails s844
microporous carbon polymers s846
Microporous materials s600, s697, s699, s820, s842, s848, s848, s966, s982, s1206, s1260
Microreactors s664, s801, s1063
Microspheres s1335
microsystems s596
Microwave s1106, s1182, s1305
microwave digestion s921
Microwave chemistry s749, s785, s1005, s1008, s1187, s1339
Microwave irradiation s1017, s1185
microwave-assisted organic synthesis s784
Michael addition s706, s720, s768, s1024, s1029, s1042, s1053, s1097, s1233, s1267, s1298, s1302
mild drying impregnation s1197
mine tailings s925
mine water s645, s925
Mine-affected river s644
mineral s692
mineral nutrition s911
mining s646
Mitsunobu reaction s1365
mixed matrix material s1090
MM/GBSA s900
Mo(VI) s962
mobility s1019
Model program s633
Modified Backbone s709
Modified Nucleobases s795
Modified Solid Phase s1106
MOFs s843
Molecular devices s698, s734, s735, s738, s873, s974, s1195, s1211
Molecular diversity s714, s768, s804
molecular dynamics s710, s817, s818, s820, s826, s844, s848, s860, s868, s874, s876, s881, s889, s1044, s1242, s1272, s1272
Molecular electronics s732, s736, s737, s743, s744, s1229, s1237, s1239, s1246, s1328, s1360
Molecular evolution s1293
Molecular Function s858
Molecular imaging s723
molecular layering s1248
Molecular logic s861
Molecular Logic Gates s943
molecular machines s734, s736
Molecular modeling s811, s819, s866, s1306
molecular motor s736
molecular motors s1044
molecular muscle s1294
molecular objects s1262
Molecular Probes s723
molecular recognition s711, s717, s732, s735, s742, s780, s798, s833, s842, s1019, s1055, s1058, s1068, s1157, s1242, s1243, s1243, s1244, s1281, s1289, s1318
Molecular rotors s1327
molecular sheets s747
Molecular switch s1259
molecular switches s734, s943
Molecular tweezers s1259
Molecular Wire s1316
molecular wires s1156
Molybdenum s733, s936, s938, s963, s978, s1095, s1187
monitoring s613, s917, s1163, s1164
monoclonal antibody s613
Monolayer s1218
monolayers s746, s783, s1247, s1258, s1346
monolayers on glass s1028
monometallic supported nanoparticles s1196
Montmorillonite-sorbitol s1248
moss biomonitoring s910
Mucin MUC1 s775
multianalyte s596
multiblock multicomponent copolymers s786
multicompartment micelles s786
Multi-component Reaction s1327
Multicomponent reactions s767, s768, s1253, s1289
Multi-component reactions s785
multidisciplinarity s620
multifunctional ligands s993
Multilateral Environmental Agreements s631
Multimetal complex s980
multiple bonding s997
multiple sclerosis s615
Multivalency s1234
multivariate curve resolution s617
Multivariate image analysis s617
Mustard Compounds s661
Mutagenesis s704

List of Keywords

mutiple bonds s871
Mycobacterium s1305
Mycobacterium tuberculosis s704
Myers-Saito cyclization s771
Myocardial ischemia/reperfusion injury s1134
N ligands s680, s694, s881, s950, s1008, s1016, s1087
N, S co-doping s1208
N,N-donor ligands s984
N,P ligands s996
N-acyl-N'-arylidene-hydrazines s1336
NADH regeneration s693
Nano-adhesion s1215
Nanocatalyst s1250
Nanocomposit s1054
nanocomposite s1039, s1209, s1254
nanodiamond s1219
Nanofibers s1229
nano-filler s1039
Nano-friction s1215
nanochannel s608
nanochemistry s743
nanomaterials s734
Nanomechanical Devices s834
Nanomembrane s867
Nanoparticle s710, s1250
Nanoparticles s590, s595, s612, s652, s678, s680, s682, s721, s730, s731, s740, s742, s746, s749, s749, s750, s751, s752, s761, s776, s806, s810, s826, s830, s845, s860, s955, s978, s990, s1017, s1036, s1053, s1097, s1159, s1196, s1198, s1207, s1214, s1215, s1220, s1220, s1226, s1227, s1228, s1229, s1230, s1231, s1231, s1232, s1234, s1236, s1239, s1240, s1241, s1244, s1246, s1249, s1250, s1254, s1256, s1257, s1257, s1260, s1262, s1309, s1335
Nanoporous material s1310
nanoscale order s744
nanoscaled Hybrid Materials s963
Nanosilica s1072
Nano-sized doped ITO s994
Nanostructure s851, s852, s1209
Nanostructures s593, s660, s685, s721, s729, s730, s732, s733, s737, s746, s752, s752, s787, s802, s820, s844, s850, s885, s946, s1037, s1038, s1040, s1210, s1213, s1214, s1216, s1217, s1221, s1222, s1226, s1229, s1231, s1246, s1247, s1251, s1260, s1328
Nanotechnolgy s1217
Nanotechnologie s1262
Nanotechnology s594, s596, s731, s743, s750, s838, s1211, s1211, s1213, s1233, s1235, s1237, s1240, s1242, s1244, s1255
nanotube s1238
nanotubes s593, s609, s612, s731, s741, s953, s1221, s1233, s1255
naphtalene s872
Napthalenediimide s1226
natural fillers s1193
natural pigment s674, s861
natural product s658
Natural products s703, s706, s716, s718, s728, s766, s778, s793, s804, s930, s1005, s1007, s1025, s1044, s1045, s1071, s1091, s1159, s1170, s1187, s1271, s1286, s1291, s1292, s1292, s1315, s1325, s1337, s1348, s1353, s1364
N-Connected Objects s834
N-donor ligands s939
Neotame s1343
NERs887
network s669
neurotransmitters s598
NHC ligands s976
N-heterocyclic carbenes s757
Ni s993
Ni alloys s1134, s1157
Ni(II) complexes s700
Ni,Cd, Pb s919
Nickel s684, s826, s911, s933, s966, s982, s1210, s1256, s1302, s1354, s1363
nickel complexes s958
nickel chloride s935
nickel(II) s934
nicotinic acid s1065, s1334
NIR s1141
nirosation s811
Nitric oxide s751, s1134
Nitrides s610, s1217
Nitrile oxides s1367
nitrite s811, s981
Nitroazidobenzene s1142, s1149
Nitrogen s1176, s1271
Nitrogen Fixation s936
Nitrogen heterocycles s694, s784, s1001, s1031, s1057, s1063, s1270, s1288
Nitrogen oxides s637, s664, s685, s945, s957
Nitrogen-doped graphene s1228
nitrosation s812
nitrosyl s981
N-ligands s1088
NLO s1034
N-methylimidazole-4,5-dicarbonitrile s1043
NMR s590, s673, s697, s717, s1027, s1340
NMR spectroscopy s617, s654, s673, s768, s782, s794, s812, s854, s881, s970, s977, s978, s983, s991, s1001, s1048, s1057, s1060, s1086, s1166, s1176, s1182, s1198, s1244, s1288, s1343, s1358
NMR titration s939, s1234
NMR-measurements s958
Noble metals s697
nodularin s598

Non linear optical properties s870
Non-aqueous capillary electrophoresis s1121
Noncovalent interactions s760, s800, s813, s1011, s1030, s1040, s1272, s1272
non-covalent interactions s610, s1099
non-linear modeling s614
Nonlinear optics s729, s782, s820
Nonstoichiometric compounds s691
Nuclear Chemistry s928, s929
nuclear magnetic resonance s704
Nuclear Waste s924
Nucleating agents s1054
Nucleic acids s1039
Nucleophilic addition s767, s1315
nucleophilic aromatic substitution s1045
Nucleophilic substitution s1345
nucleophilic vinylic substitution s770
nucleophilicity s958
nucleosides s604, s831, s1003, s1011, s1045, s1073, s1318, s1323
nucleosomes s713
nucleotides s604, s857, s1111, s1229, s1364
Nucleus-independent chemical shift (NICS) s986
Nylon s802
o- effect s1131
O ligands s983
O2 plasma s1201
octadecyltrichlorosilane s849
ofet s1322
oil products s1149
Oled s1028, s1321
OLEDs s937
olefin s592
olefin metathesis s976
olefination s1050
Oleic acid s926
Oligoene s806
oligomeric macrocycles s1334
oligomerization s1328
oligonucleotides s712, s724, s1003, s1233
oligosaccharides s723, s1027
oligothiophene s1019
O-O activation s686, s955, s1087, s1304
OPE s1316
operando s810
optical activity s753
optical spectroscopy s1083
optimization s1124
Ordered mesoporous carbon spheres s959
organic catalysis s784
Organic Electronics s773, s1300, s1360
organic field-effect transistor s1019
Organic field-effect transistors s1201
Organic Chemistry s667
Organic Materials s842
Organic matter s651
organic peroxides s1279, s1356
Organic photovoltaics s790
organic semiconductors s1019
organic solar cells s773
organic-inorganic hybrid composites s699, s955, s1303, s1319
Organocatalysis s735, s758, s774, s782, s853, s1010, s1012, s1020, s1024, s1029, s1046, s1047, s1064, s1085, s1097, s1233, s1264, s1269, s1287, s1289, s1292, s1298, s1310, s1317, s1336, s1338, s1356, s1361
Organocatalyst s1277, s1284
Organometallic s939, s1277
organometallic mixed-valent chemistry s1156
organometallics s766
organozinc s939
origin s673
oscillatory reaction s1144
Oxidant s987
oxidation s589, s596, s663, s683, s706, s707, s708, s725, s783, s803, s806, s902, s905, s977, s987, s992, s1029, s1041, s1072, s1076, s1114, s1165, s1186, s1188, s1203, s1226, s1276, s1290, s1298, s1304, s1357
oxidation state s922
Oxidations s658
Oxidative damage s907, s918
oxidative dehydrogenation s1248
Oxidative stress s918
Oxides s947
Oxidoreductases s704, s706
Oxo Cluster s1236
oxone s688
Oxygen s1007, s1134
Oxygen evolution s984
Oxygen evolving complex s984
Oxygen heterocycles s610, s1086
Oxygenation s708
ozone s905
ozonolysis s725, s1045
P ligand s945
P ligands s1014
PAH s917
Palladiujm s941
Palladium s663, s696, s697, s754, s774, s806, s932, s950, s960, s977, s978, s981, s1002, s1012, s1014, s1018, s1042, s1051, s1065, s1067, s1070, s1080, s1094, s1222, s1226, s1230, s1273, s1285, s1307, s1312, s1315, s1349, s1357, s1361
Palladium catalyzed Epoxide Opening s998
palladium cytalysed cross-coupling s1093
Para hydrogen s1340
Para hydrogen induced polarization s1340
paraoxonase s907
Partial Least Squares s1141
passivation s1222
passive remediation s642
Patulin s1140
Pb(II) adsorption s1192
PbO2 s906
Pd catalyzed reaction s1083
Pd-catalyzed O?C allylic rearrangement s1319
Pd-Ni-P s1205

PDT application s979
Peach processing s1161
Pedot s1212
pentacene s1201, s1322
Peptide s715, s717, s776, s1106
Peptide Nucleic Acid s709, s795
Peptides s613, s705, s711, s711, s720, s724, s726, s785, s853, s874, s879, s887, s1004, s1085, s1164, s1168, s1298, s1364, s1367
Peptidomimetics s720, s772, s1050, s1291, s1343
Pericyclic reaction s791, s819
periodic acid s1340
Periodic mesoporous organosilica s841
periodic network s747
Perlite s647
pernitride s851
perovskite s948
Perovskite phases s1240
peroxidase s907
peroxide s884
Peroxides s683, s1007, s1304
peroxyoxalate s1279
perylenediimides s1212
pH s748
pH induced changes s1215
Pharmaceutical s1117
pharmaceuticals s648, s650
Pharmacophore s900
pharmacophore model s1018
Phase diagrams s662, s882
phase transformation s969
Phase transitions s835, s881, s882
phase-transfer catalysis s758, s1020, s1024
phenol s1013
phenolic acids s1151
phenolic compaunds s907, s918
phenolic compounds s1119
Phenolics s1161
phenylboronic acid derivative s1232
Pheromones s930
Philosophy of chemistry s626
phonon confinement effects s1245
Phosphane ligands s679, s695, s938, s948, s1198, s1308, s1363
Phosphanes s947
phosphasilapropene s997
Phosphate s1280
Phosphine s941
phosphine borane s1060
Phosphines s1070, s1071
Phospholipids s894, s1299
phospholipids vesicles s886
Phosphonomethionine s1046
Phosphorescence s1028
Phosphorous ligands s1022
phosphorus s747, s773, s946, s960, s965, s967, s1000, s1008, s1070
Phosphorylation s1069, s1278, s1299
photoactivation s839
Photoaffinity labeling s727
Photocages s750
photocatalysis s660, s910, s975, s976, s990, s1041, s1084, s1087, s1180, s1286, s1310
Photocatalytic Hydrogen Evolution s1175
photocatalytic property s1209
Photodynamic s1112
Photodynamic theraphy s969
photodynamic therapy s986, s988, s1214
photo-electrochemistry s693
photoelectron spectroscopy s825, s854, s877
photochemical hydrogen evolution s988
Photochemistry s627, s649, s681, s698, s701, s714, s726, s738, s783, s788, s808, s871, s943, s947, s974, s981, s996, s1003, s1041, s1047, s1049, s1074, s1173, s1174, s1225, s1231, s1346, s1352
Photochromism s738, s746, s750, s780, s968, s1225
photoisomerization s738
photoluminescence s742
Photolysis s649, s904
photooxidation s730
Photophysics s699, s738, s746, s781, s815, s828, s830, s938, s967, s988, s1225, s1353
Photoprotein s1270
photoredox catalysis s1041
Photoremovable protecting groups s1265
photoresponsive behavior s1034
Photosensitizer s988
Photostimulated luminescence s1167
photoswitchable monolayers s1028
Photosynthesis s832
photosystems s804
Phthalates s1163
Phthalocyanine s986, s987, s987, s988
Phthalocyanines s956, s969, s971, s1225, s1279
PHWE, s1131
Physical Chemistry s667
Phytoextraction s911, s911
Phytohormones s856
Phytochemistry s1170
phytoremediation s911
P-chiral secondary phosphine oxides s1015
Pi interactions s1012, s1326, s1328, s1335
picolinic acid s1065, s1334
pincer ligands s700
piroxicam s1144
pit lake s925
pKa prediction s859
plasma chemistry s1179
platencin s719
platensimycin s719
platform s1095
platform concept s1294
Platinabenzene s986
Platinum s679, s697, s713, s932, s949, s959, s967, s1102
platinum deposition s1133
platinum nanoparticles s1181
platinum(II) complexes s940
plga s1214
Pnicogens s946
p-nitrophenyl glycoside s1027
polarization s821
pollution s645
Poly(ethylene) s1104
Poly(vinyl alcohol) s1335

Poly(vinyl triazole) s1365
polyacetylene s764
Polyacrilonitrile derivatives s1062
Polyalphaolefin s1105
polyanion s787
Polyanions s718
polyaromatic hydrocarbon s1281
polyaromatic hydrocarbons s1266
Polycaprolactone s793
polycyanurate s1015
Polycycles s1098, s1276, s1326, s1333
Polycyclic Aromatic Hydrocarbon s806
polydiacetylene s1287
Polydimethylsiloxane s793
polyelectrolyte s1252
Polyethyleneimine s1080
polyferrocenosilane s954
polyglutamic acid s1027
Polyhalides s836
Polyketides s1358
Polymer s1015, s1034
Polymer Gel s1080
Polymer Micelles s750
polymeric nanocomposite s1247
polymerization s595, s788, s880, s955, s965, s998, s1005, s1038, s1048, s1066, s1067, s1095, s1099, s1102, s1103, s1105, s1182, s1262, s1297, s1300, s1310, s1319, s1325
polymerization in dispersed systems s792
polymerizations s688
polymers s599, s600, s612, s656, s685, s750, s752, s769, s786, s788, s789, s791, s793, s857, s882, s946, s998, s1000, s1004, s1007, s1025, s1034, s1036, s1037, s1049, s1052, s1058, s1067, s1099, s1151, s1153, s1161, s1184, s1192, s1239, s1244, s1253, s1262, s1266, s1268, s1269, s1282, s1291, s1293, s1296, s1297, s1319, s1321, s1338, s1341, s1353, s1355
Polymorphism s1204, s1307
Polynuclear s933
polyoxometalate s681, s942, s989, s993, s1203, s1239, s1250
polyoxometalates s666, s697, s697, s715, s733, s933, s961, s984, s992, s992, s1254, s1319
polyphenol oxidase s907, s918
polyphosphazenes s688
polypropylene s1039, s1248
polyrotaxane s735
Polyurethane block copolymers s1105, s1366
Polyvinylpyyrolidone (PVP) s1115
poplar s911
Porous networks s842
porous silicon s742
Porous solids s843
Porphyrin s678, s1207, s1252, s1351
Porphyrinoids s732, s817, s1016, s1040, s1060, s1072, s1185, s1225, s1278, s1350, s1360
portfolio s927
potentiometric s1144
potentiometric selectivity s593
Potentiometry s1125
powder x-ray diffraction s847
p-quinol s1059
practical exercise s929
Precaution s676
precipitation s907
prenylated compund s1013
preparing temperature s1201
primary alcohols s802
Principal Component Analysis s617, s1160, s1166
process intensification s656
prochiral ketone s1094
pro-oxidant s674
propargylamines s784
Propargylic alcohols s1073
Propylene Glycol s1110
Protecting groups s854, s891, s1086
Protective Groups s1286
protein s606, s717
protein aggregation s896
protein design s1367
Protein engineering s590, s608
Protein expression s1267
Protein modifications s796
protein regulation s885
protein structures s855, s889, s891
Protein surface s717
Protein-protein interactions s891
Proteins s590, s599, s885, s902, s1069, s1165, s1256
proteomics s602, s613, s726, s727, s728
protic solvents s1334
proton acceptor s690
Proton transport s1026, s1270
Protonation s782, s830
proton-catalyzed s1266
pseudo-first order s1092
Pseudorotaxanes s1234
Pt(0) s1241
p-tert-butyl calix[6]arene derivatives s1344
p-type Gallium Arsenide s693
Public Image s629
Push-pull chromphores s1043
Pymerization s1425
Pyrazinamide s1305
pyrazinoquinoline s770
pyrazole s1294
Pyrazolidine s1016, s1331
pyrazolo[3,4-d]pyridazine s1294
pyrimidine salts s1356
pyrimidinophane s1334
pyrimido[4,5-b]indole ribonucleosides s1093
pyrimidopteridines s1077
Pyrolysis s1366
pyrolytic carbon s659
Pyronine Y s1112
pyrrolidine iminosugars s1359
pyrrolo[1,2-b]pyrazoles s1359
QM/MM s816, s821
QM/MM simulations s863
qsar software s1359
quantitative structure-property relationship s874
Quantity injection s1147

Quantum dots s742, s748, s748, s750, s829, s1211, s1245
Quantum Chemistry s686, s813, s815, s822, s864, s876, s878, s991, s1176
Quaternization s988
quenching s748
quercetin s674
Quinoline s971
quinoline-2,4-diones s1342
Quinones s649, s1123
quntum-chemical calculation s809
radical s674
Radical cascades s771
radical reactions s767, s771, s863, s1075, s1298, s1305
radicals s835, s952, s1084, s1169, s1241, s1271
Radioactive cesium s636
Radioactive contamination s636, s920
Radiochemistry s635, s637, s638, s640, s720, s924, s928, s931
Radiopacity s1335
radiopharmaceutical s715
radiopharmaceuticals s709, s717
radium-226 s920
radium-228 s920
RAFT polymerization s748
Raman spectroscopy s606, s826, s828, s862, s893, s1154, s1154, s1219, s1228, s1333
Rare Earth Elements s640
rare earths s788, s991, s1206, s1336
Raschig process s1331
Rat heart model s1134
rate constants s952
Reaction Mechamisms s819
reaction mechanism s688, s821
Reaction mechanisms s652, s686, s686, s690, s746, s816, s822, s880, s882, s949, s1024, s1051, s1302, s1317
Reaction Order s1344
reaction pathways s824
Reaction Rate Constant s1344
reactive intermediate s688
reactive intermediates s685, s764
Reactivity s682, s972
rearrangement s610, s670, s695, s821, s1313
rearrangement reactions s1023
Receptors s778, s1222, s1290, s1296, s1331, s1356
reclamation s925
recycling s1015
Red mud s908
redox cycles s958
redox chemistry s596, s686, s688, s902, s1074, s1123, s1145, s1188, s1272, s1341
Redox processes s639
Reduction s652, s758, s865, s947, s960, s1087, s1145, s1191, s1257, s1342
Reflectometric interference spectroscopy (RIfS) s1129
reforming s1219
regioselectivity s765, s799, s823, s865, s1045, s1068, s1077, s1273, s1274, s1316
rechargeable battery s1106
Relativistic effects s813
renewable s1015, s1182
renewable resources s653, s675, s1025, s1094, s1178
Research funding s633
retention s923
Reverse Micelle s1115
reversible addition-fragmentation chain transfer s792
Rhenium s983, s996
Rhenium(IV) s994
Rhodium s652, s694, s1312
Ribozymes s872
Rifampin s1137
rigid polyurethane foam s1054
rigid-rod polymer s1320
ring closing metathesis s1048
Ring expansion s764
ring opening metathesis polymerization s846
Ring-opening polymerization s788, s1004, s1291
Rio Earth Summit s631
Risk s676
risk management s620
river bottom sediments s920
River water s1140
RNA s876
Rotaxane s1233
Rotaxanes s729, s735, s797, s1026, s1085, s1211, s1225, s1241, s1272, s1272
Ru(II) complexes s1214
Rubrerythrin s888
Ruthenium s592, s678, s684, s685, s696, s699, s716, s758, s826, s830, s862, s882, s938, s943, s944, s947, s976, s1014, s1023, s1032, s1082, s1156, s1173, s1198, s1220, s1308, s1316, s1351, s1352
S Ligands s936
Saccharide probe s861
Salt Bridge Containing Polar Pocket s898
salt effect s1164
salt spray environment s1118
Samarium s1271
Sandwich complexes s873
sausage s677
scanning Kelvin probe microscopy s849
Scanning probe microscopy s927, s1058
scanning tunneling microscopy s745, s1032
Scatchard Plot s1113
science s619
Scientific responsibility s629
Sclerotinia sclerotiorum s885
Screening s1028
seawater s635
secondary batteries s1107
sector model s859
sediment s917, s918
Sedimentary archive s644
selective solvents s786
selediazoloquinoline s770

selenium s652, s923, s1147, s1312
Selenophene s1300
Selenophene Ring Fragmentation s1300
Self assembly s1038, s1335
self evaluation s623
Self-assembl s1033
Self-Assembled 3D Crystals s834
self-assembled monolayer s1201, s1424
self-assembled monolayers s745, s1032
Self-assembly s729, s732, s733, s737, s743, s744, s746, s752, s780, s791, s792, s794, s794, s798, s805, s809, s810, s833, s835, s836, s953, s954, s985, s989, s1008, s1012, s1030, s1081, s1089, s1093, s1211, s1216, s1217, s1224, s1229, s1246, s1247, s1251, s1252, s1254, s1258, s1272, s1303, s1324
Self-healing s833
self-organization s744
self-study training s929
semiconductors s742, s781, s789, s996, s1061, s1192, s1326, s1362
semiempieical calculations s1362
sensing s796
Sensitizers s649
sensor s1111
Sensors s595, s611, s612, s797, s802, s1118, s1122, s1143, s1213, s1214, s1224, s1243, s1256, s1341
Separation s1351
separation strategies s603
sequential injection analysis s605
Serbia s907
service oriented s623
sewage sludge s925
shape persistence s1262
shape-persistent macrocycles s745
shape-persistent molecules s1032
Schiff base s1131
Schiff bases s799, s812, s847, s896, s954, s956, s991, s1293
Schiff-base s1265
schwertmannite s903
Si ligands s702
sialic acids s775
Signal enhancement s1340
Silanes s755, s769, s970, s985, s1051, s1221, s1354
silica s1090
Silica fume s908, s914
silica hydride material s1151
Silicates s1200, s1217
silicon s689, s702, s742, s754, s913, s964, s965, s967, s1221, s1242, s1260
silicon analysis s1157
Silicon based s1277
Silicon- based s1264
silicon nanocrystals s742
silicon tetrachloride s935
Silver s679, s968, s1073, s1231, s1234, s1235, s1247, s1257, s1273
Silver bromide nanocrystal s1209
Silver nanoparticles s1135, s1219
Silver Vanadium Oxide s953
silyl cations s1266
singet oxygen s751
single crystal diffraction s1125
Single-molecule studies s736, s743, s882, s1078
Singlet oxygen s649, s969, s986, s1014, s1225, s1239, s1279
single-wall carbon nanotubes s1105, s1366
six carbon (6-C) synthon, 2,2’-bisallyl diradical s1057
skills s929
skutterudite s851
Small ring systems s777
SMART X2S s1125
smokeless powder s1124
sodium s1164
software package GIS-INTEGRO s910
soil s1149
sol gel s904
solar cells s1212
Solar Energy Conversion s803
Sold-Phase Peptide-Synthesis s711
Sol-gel s1137
Sol-Gel Process s1213
Sol-Gel processes s682, s699, s730, s966, s1200, s1201, s1220, s1237, s1249, s1366
Solid acid catalyst s659
solid catalysts s1092
solid electrolyte s948
solid phase s884
solid state chemistry s839
Solid state photopolymerization s1320
Solid state structures s848, s1206
solid superacid s1177
solid/liquid interface s1032
solid/liquid-interface s745
Solid-phase synthesis s713, s716, s749, s772, s775, s891, s1002, s1111, s1112, s1367
solid-state chemistry s656
Solid-state reactions s836, s837, s966
Solid-state structures s814, s835, s837, s838, s959, s967, s1202, s1345
Solubility s971
solutions s827
solvated electron s604
Solvent effect s1141
solvent effects s815, s870, s1303, s1304
Solvent free s1295
solvent properties s958
solvent-free conditions s663
solvent-free synthesis s656
Solvolysis s1030, s1040
solvothermal synthesis s994
Sorption s651
South African Education s630
Soxhlet extraction s1124
speciation s639, s646, s924
spectroelectrochemistry s1156
spectrometric detection s603
spectroscopic investigation s1252
spectroscopy s807, s890
Spent Bleaching Earth s915, s915
Spent catalysts s1187

List of Keywords

Spent Nuclear Fuel s924
Spin crossover s680, s698, s736, s951, s974, s980
Spinel phases s1231
Spiro compound s803
Spiro compounds s1098, s1313
spme s601
SPME-LC/MSn s1116
spray deposition s657
Spray-ILGAR s1222
squaramide s1338
Square wave voltammetry s1137
squid s995
stability s884
stable intermediates s952
Stacking interactions s795, s845
staff development s633
static/dynamic light scattering s786
stationary phase s857
stationary phases s1115
Statistical thermodynamics s666
stereochemically s1200
Stereochemistry s858
Stereoselective Epoxidation of Enals s998
Steric hindrance s695
steroid s1066
steroids s778, s833, s855, s1006, s1006, s1035, s1035, s1076, s1076, s1089, s1101, s1278, s1301, s1307, s1333, s1350, s1350, s1367
Stockholm Convention on Persistent Organic Pollutants s631
stockings s620
storm water s648
strained molecules s714
stress-strain properties and structural parameters s1105, s1366
Strontium s919, s1187
strontium determination s921
Structural Biology s590, s704, s855, s898
structural dynamics s827
Structural Genomics s590
Structural properties s994
Structure s682
structure elucidation s602, s680, s725, s893
structure characterization s850
structure prediction s851
structure variation s814
structure-acidity relationship s654
Structure-activity realtionships s1339
Structure-activity relationships s727, s778, s860, s902, s1170, s1330
STT-type zeolite s849
subcritical drying s1189
Subsidy Driven Research s630
substituent effect s986
Substituent effects s699, s808, s1051
Substituents effects s1288
Substituted Styrenes s1022
sucrose s1075
sugars s807
sulfamethoxazole s1183
Sulfamide-Ligands s1306
sulfinylimidate s1010
Sulfonamides s904, s1114, s1290
sulfonation s659, s787
sulfoxidation s1356
Sulfur s641, s913, s1043, s1067
Sulfur heterocycles s773, s781, s798, s965, s1155
Sulfur oxides s664
sulphonamide s1294
Sunflower s911
superbase s1313
superconductors s1199
Supercritical fluid s1227
supercritical fluids s666, s1190
Supported catalyst s1250, s1250
Supported catalysts s788, s1207, s1251
Supramolecular s1218, s1352
Supramolecular complexes s1110
supramolecular electronics s743
Supramolecular chemistry s611, s697, s700, s730, s731, s733, s734, s739, s743, s768, s780, s794, s795, s798, s800, s802, s805, s833, s837, s838, s858, s881, s887, s938, s947, s953, s1001, s1003, s1008, s1012, s1019, s1026, s1030, s1040, s1047, s1058, s1058, s1068, s1078, s1081, s1088, s1093, s1096, s1102, s1102, s1118, s1190, s1211, s1216, s1218, s1222, s1223, s1225, s1229, s1239, s1241, s1242, s1242, s1243, s1243, s1249, s1252, s1258, s1259, s1296, s1318, s1331, s1354, s1360
supramolecular ligand s897
supramolecular species s940
surface analysis s612, s848, s964, s1000, s1240, s1255, s1366
Surface chemistry s783, s792, s824, s825, s838, s860, s964, s1037, s1198, s1252, s1258, s1318, s1335
Surface patterning s793
surface plasmon resonance s1260
Surface science s808
surface water s917
surface-initiated polymerization s804
Surfactants s597, s780, s791, s826, s879, s1062, s1269
Sustainability s640, s671
sustainable food production s672
Sustainable Chemistry s630, s661, s701, s756, s773, s853, s914, s947, s964, s981, s1014, s1082, s1173, s1174, s1191, s1235, s1268, s1339
Suzuki coupling s1348, s1359
Swimmers s744
switchable solvents s1178
Synchrotron s903
synthesis s791, s856, s899, s987, s1027, s1262, s1265, s1334
Synthesis design s703, s722, s737, s769, s777, s785, s855, s857, s892, s1016, s1043, s1060, s1070, s1103, s1192, s1267, s1306

synthesis route s948
Synthetic Biology s796
synthetic carbon allotrope s741
Synthetic design s1108
synthetic methods s703, s759, s761, s764, s766, s768, s768, s774, s796, s854, s942, s1000, s1001, s1009, s1010, s1020, s1025, s1030, s1096, s1100, s1103, s1103, s1202, s1202, s1278, s1291, s1299, s1302, s1323, s1350
Synthetic vaccines s775
T2 toxin s1162
Table Olive Processing Wastewater s916
tandem mass spectrometry s1132
Tandem reactions s1337
target recognition s1232
teaching s634, s930
teaching competency s929
Teleme s1160
Tellurides s852
TEM s994
Template syntheses s841
Template Synthesis s799, s840, s1040, s1085
templated self-sorting s804
Terbium Complexes s943
Terpenoids s930, s1108
terpyridine coordination compounds s781
tertiary alcohol s763
test method s1134, s1157
tetrahydrofuranyl ethers s1023
Tetrasubstituted stereocenters s771
tetrazole s1332
texture s617
TG s1142
therapy s751
Thermal analysis s1149, s1344
thermal conductivity s1054
Thermal conductivty s1188, s1194
Thermal Decomposition s1142
thermal treatment s1195
thermodynamic and redox stability s886
Thermodynamic equilibrium calculation s636
Thermodynamic stability s607
thermodynamics s671, s870, s899, s1099, s1179, s1199, s1202
Thermoelectric s852
thermoelectric materials s1256
thermoelectrics s851
Thermochemistry s1178
Thermoluminescence s1167
thermoset s1015
Thiadiazolo Benzamide s883
thiazol derivatives s982
Thick Film s1147
thin film solar cells s1222
Thin films s802, s1156, s1217, s1237, s1240, s1255, s1255, s1338
thiobenzanilides s874
thiophene s773, s1043
Thiophosphate s1280
thioredoxin system s704
third generation photovoltaics s657
Thrombin s1127
time-resolved spectroscopy s699, s704, s828, s830, s864, s877
Tin s955, s1163
TiO_2 s1183
TiO_2 nanotube arrays s1175
TiO-PAN s922
titania s910
titanium s755, s767, s964, s993, s1251, s1252
titanium oxide s923
Titanium-catalyzed s1306
Titaniumu dioxide photocatalyst s1208
topochemical polymerisation s1287
topochemical reaction s747
topochemistry s1235
Topological Control s834
Total synthesis s719, s759, s759, s766, s778, s1005, s1010, s1045, s1278, s1302, s1319, s1350, s1353, s1367
Toxicity s650
toxicology s646, s909
Trace analysis s1138, s1143
Trace metal s918
training s928
Transcription factors s711
transferases s822
Transferfactor s911
Transformation products s650, s904
transition metal s810
transition metal catalysis s762
transition metal complexes s982
transition metal nanoparticles s952
Transition metals s642, s651, s695, s702, s759, s912, s913, s945, s948, s968, s992, s1169, s1297, s1336, s1355
Transititon metal complexes s1126, s1127
transmembrane-peptide s1232
transmission electron microscopy s786, s1256
triazine s1101
triazole s1322
Triazole derivatives s1347
Triazoles s1309
Triclosan s693, s905
tricyclic analogues of purines s1365
Tridentate ligands s736, s961, s1302
triethylaluminum s1311
trilobolide s1035
tripodal ligand s940
Tripodal ligands s977
Tripodal Phosphane Ligands s936
Tuberculosis s1305
Tumor growth s1150
Tungsten s945
tungstoarsenate s989
Tunnelling s845
Twin Polymerization s963
two-photon absorption s1214
tyramine s812
Ullmann-Goldberg mechanisms s975
ultra high performance liquid chromatography s1132
ultrafast s827
ultrafast spectroscopy s829
ultramicroelectrode s1126
Ultrasound s1187
ultrasounds s1191

ultraviolet absorption maximum s1065, s1334
Umpolung s765
Unsymmetrical Phthalocyanine s979
up-conversion s1206
uracil s1334
Uracil derivatives s795
uranium s643, s922, s922, s923, s924
urethane formation s1309
urethane-triazole s1309
USA 300 CA-MRSA s890
UV / Vis spectroscopy s605
UV measurements s1066
UV photochemical generation s1147
UV treatment s650
UV/Vis spectroscopy s649, s684, s808, s870, s881, s895, s945, s951, s1035, s1060, s1088, s1089, s1114, s1116, s1124, s1141, s1145, s1159, s1161, s1165, s1170, s1327, s1333
Uv-vis s639
UV-Vis spectroscopy s1237, s1255, s1317
vacancy formation s814
Valence isomerization s698, s951
Vanadates s984
vanadium s666, s686, s956, s981, s1177
Variable Selection s615
VCD s1357
Vegf s1150
Vegf-R1 s1150
VEGFR2 tyrosine kinase s898
Vermiculite s647
Vesicles s879, s1224, s1243
vibrational contributions s870
Vibrational spectroscopy s606, s818, s826
vinylallene s1263
vinylic nucleophilic substitution reaction s1092
Vinyltriethoxysilane s1072
Viologen s1425
virtual campus s624
virtual community s623
virus s608
Viruses s731
visible light s1084, s1183, s1310
visible-light photocatalysis s1031
vitamin C s907
Vitamins s864
Vitrification s919
volatile form s1147
Voltammetry s595, s597, s597, s1109, s1117, s1135, s1140, s1146, s1156
Wacker oxidation s1319
washcoat s655
Waste incineration s636
Waste prevention s917, s1194
waste water treatment s693, s905
wasterwater, red mud s905
wastewater s648, s908, s908, s914, s1110
water s663, s914
Water chemistry s641, s641, s643, s645, s675, s733, s771, s1021, s1080, s1190, s1201, s1270, s1339, s1345
water intrusion-extrusion experiments s849
water reduction s949
Water splitting s701, s739, s944, s949, s1173, s1174, s1185
water-adding quantity s1208
water-hexane impregnation s1196
waterproofing s1193
water-soluble ions s907
wavelets s617
wax esters s1130
wet chemistry s922
WHAM model s650
White phosphorus s679
white-brined cheese s1160
Wide Angle Scattering s903
withasomnine s1359
Wittig reaction s1001
women s620
writing s667, s667
xanes s922
XANES/EXAFS s639
Xanthene s1265
xenon s845
XPA/Rad14 s887
X-ray s827
X-ray absorption spectroscopy s1220
x-ray absorption pectroscopy s825
X-ray absorption spectroscopy s637, s638, s830, s1249
X-ray crystallography s893
X-ray diffraction s654, s782, s799, s832, s837, s848, s892, s936, s973, s977, s979, s983, s991, s1137, s1176, s1188, s1204, s1208, s1213, s1240, s1249, s1272
X-ray difraction s991, s1232
X-ray fluorescence s1132
X-ray photoelectron spectroscopy s1424
X-ray techniques s639
yeast extract s885
ynol ether s1010
young chemist s669
zeolite s919
Zeolites s654, s848, s966, s1199
Zeta potentiel s1138
zinc s645, s686, s754, s939, s971, s986, s988, s1232
zinc alkyls s690
zinc hydroxide s690
Zinc isotopy s644
zinc oxide s975
zinc selenide s1245
Zirconia s609
Zirconium s966
Zn(II) coordination polymers s781
ZnO s1054, s1195
ZnS nanodots s1222
Zwitterions s737

Theoretical Chemisry – I

O-527

SINGLET FISSION FOR EFFICIENT DYE-SENSITIZED SOLAR CELLS

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Singlet Fission is a spin-allowed process in which a molecular chromophore excited into its singlet state shares energy with a nearby ground state chromophore, producing a pair of triplet excited chromophores initially coupled into an overall singlet. In a more detailed description, the initial singlet state actually is a coherent superposition of eigenstates of the total Hamiltonian operator that includes electron spin-spin and Zeeman interactions that dictate its further fate, along with possible spatial diffusion, internal conversion, intersystem crossing, and other possible competing processes.

Although, the Singlet Fission is known is some special cases of crystalline aromatic hydrocarbons for a half of century, using of this process for increasing of the solar cell efficiency is a new topic. It includes studies of several steps and interplay of theoretical, synthetic, and spectroscopic procedures, namely:

- Selection of the proper chromophore which satisfies the following conditions: $E(S\ 1) \geq 2\ E(T\ 1)$ but also $E(T\ 2) \geq 2\ E(T\ 1)$. We have observed that 1,3-diphenyl-isobenzofuran satisfies these conditions and yields 200 % of triplet states in a crystalline state.
- For practical reasons, the S 1 excitation energy should be around 2.2 eV. Searching for structures with this property is done by extensive set of quantum chemical calculations of excited states. We have already preselected a few structures which have to be now synthesized and studied experimentally.
- For effective Singlet Fission process proper mutual orientation of chomophore pairs is essential. We have developed a simple Hamiltonian model and performed numerical calculations for different orientations of chromophores. The rules for the geometrical requirements resulted from these calculations will be discussed.
- Preparation of a dye with both chromophores in ideal positions, either by self-organization or by synthesis of supermolecule with both chromophores properly arranged in it.
- The final stage requires separation of charges of individual triplet chromophores, transport of the charges to the $TiO\ 2$ semiconductor and injection of the electrons to the semiconductor.

We will report on progress in the first three steps, the last two steps still need to be solved.

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DIRECT ALKYLATION OF GOLD SURFACE

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We report methods for ambient solution coating of a gold surface with a self-limiting monolayer containing alkyl chains attached by one or more C-Au bonds, and no other elements. The alkyl transfer agents are alkyl derivatives of metals such as Sn, Hg, Ge, and others. This is a generalization of our previous finding that under ambient conditions solutions of alkylated stannanes deposit alkyl-containing monolayers on gold surface,[1] and is in accord with break-junction conductivity measurements on single molecules attached to gold through carbon by transfer from trimethylstannyl derivatives.[2]

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Keywords: *Self-assembled monolayer; X-ray photoelectron spectroscopy; Cyclic voltammetry; Electrochemical impedance spectroscopy;*

P-1020

PURPLE-TO-TRANSMISSIVE ELECTROCHROMIC SWITCHING OF VIOLOGEN-BASED DENDRIMER

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The growing threats brought about by climate changed promoted by human activities have gained a large amount of serious attention from both the private and government sectors. Climate change brought about by manmade emissions of CO_2 by the combustion of fossil fuels has many consequences associated with it, including drought, more violent storms, and de-glaciation just to name a few. Curtailing CO_2 emissions is a major objective to achieve in order to mediate against these threats. So-called smart windows based on electrochromic materials offer a promising way of regulating the amount of light permitted to enter a building. Towards this end we have designed a viologen(BIPY 2+)-based dendrimeric material that has, under its reduced form, significant absorption in the UV, visible, and near infrared regions of the solar spectrum. The ability of two BIPY•+ radical cations to undergo π-dimerization (also known as pimerization) is driven by radical-radical interactions mostly involving spin pairing of the two spins into a singlet state. As a consequence of dimerization the absorption band characteristic of viologen radical cation at ~600 nm becomes blue-shifted, resulting in a purple color, and a significant absorption band in the NIR region of the spectrum emerges. In the case of methyl viologen radical cation, this dimerization only occurs at relatively large concentrations or low temperatures in MeCN solutions. A large amount of research efforts has gone towards enhancing the stability of these dimers in solution, including host-guest chemistry, mechanostereochemistry, and covalent preorganization. Herein, we present a strategy of covalent preorganization in a viologen dendrimer containing six viologen units. The electrochromic properties of our dendrimer were first investigated in solution using electrochemistry, UV-Vis-NIR and spectroelectrochemistry. The switching ability of the hexa-viologen dendrimer was then tested on ITO electrodes. The prepared window exhibited a reversible color change from transparent to purple upon reduction.

Keywords: *Electrochromic; Viologen; Dendrimers; Pymerization;*

P-1021

NEW BIOMEDICAL AND TECHNICAL APPLICATIONS OF NANOMATERIALS

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Advances in nanoscience make it possible an unusual progress in biomedical applications.

It concerns also our current studies. Non-specific, physicochemical interactions of polymer micro- and nanofibrils with biomolecules and whole living cells lead to a number of important biomedical applications in diagnostics and tissues engineering (nanomedicine), microbiology and biotechnology. These will be discussed with regard to interaction and analysis of bioactive molecules and biomarkers (nanosensors), as well as living cells (nanobiodetectors), including detection of cancer cells, bacteria and spores. Modifications of polymer nanofibrils lead to highly-specific interactions giving better sensitivity and more specific response. Fast and sensitive devices for detection of bacteria and spores are of particular interest for health care, security and defense.

A network of polymer micro- and nanofibrils was used as a 3D scaffold for cell culture in vitro. New material and technique can be applied not only in tissues engineering, but also in large scale bioreactors.

These problems will be presented basing on the results of our newest experiments.