INTERNATIONAL CONFERENCE ON SUPRAMOLECULAR SCIENCE & TECHNOLOGY

"Supramolecules: Design and Funcionality on a Nanomolecular Scale"

ICSS&T 2004 CONGRESS

ABSTRACT BOOK

Pavel Drašar, Vladimír Pouzar and Petr Holý, Editors

PRAGUE, September 5 - 9, 2004

Venue - ICT Prague

Organizers:

Czech Chemical Society
Global Supramolecular Chemistry Network (GSCN)
Institute of Organic Chemistry and Biochemistry AS CR, Prague
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ADSORPTION AND DIFFUSION KINETICS OF ALKANES (C_3 & C_5) ON DIFFERENT CaA ADSORBENTS

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The adsorption and diffusion kinetics of propane and pentane on A molecular sieves having different degrees of calcic exchange (0, 33, 44, 57, 75% of Ca^{2+}) have been studied by thermogravimetry under a constant pressure of 27kPa and at both 373 and 523 K. The capacities of nitrogen adsorption at 77 K are respectively 0, 0.02, 0.165, 0.216, 0.222 cm^3/g for the adsorbents A_0, A_{33}, A_{44}, A_{57}, A_{75}. For both molecules, propane and pentane, the adsorbed quantities after 4 hours increase with the exchange degree. On the other hand, despite the smaller size of propane molecules ($Ø_{kinetic}$=4.3 Å) as compared to pentane ($Ø_{kinetic}$=4.9 Å), the uptakes are largely more important for pentane.

This result, found by other authors[1, 2], is due to the interaction force between the adsorbed molecules and the wall of zeolite α cavity. The interaction becomes more important when the molecular diameter increases. The adsorptions of propane at 373 and 523 K show that the increase of calcic exchange degrees affects significantly the initial rate of adsorption. It appears, consequently, that the propane can be considered as an excellent probe molecule for the characterization of calcic exchange degrees on this zeolite type. On the other hand, a model resulting from second Fick's law describes correctly the diffusion kinetics of both linear paraffins (propane and pentane).

The agreement observed between the experimental and theoretical curves is however more marked at 373 K. Indeed at 523 K, a very intense disruption of kinetics is monitored. This phenomenon is related to the diffusion difficulty, but also to a probable heavy compound formation. The good agreement between the theoretical and experimental curves at 373 K gives a better approximation approach of the diffusion in this type of zeolite and in particular with the short time approximation method.

The hypothesis that only inter-crystalline resistance is present, as it is described in literature, can be drawn aside[3]. Actually, the study of diffusion at short time highlights the effect of calcic exchange degrees on the time preceding the effective diffusion in A adsorbent.

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STEREOCHEMICALLY-TRIGGERED NONCOVALENT ADDUCT FORMATION AND DISSOCIATION OF DIASTEREOMERIC COMPLEXES IN THE GAS PHASE INVESTIGATED BY ELECTROSPRAY IONIZATION MASS SPECTROMETRY

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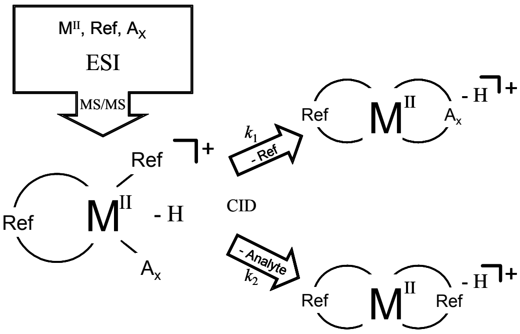
Electrospray ionization mass spectrometry (ESI-MS) is a powerful instrumental technique that has found extensive use in the analysis of various noncovalent complexes. Use in this context is attributed to ESI-MS being a soft ionization technique which imparts only modest internal energy into molecules and molecular clusters upon conversion from solution phase to gas phase[1]. In the case of different molecules which possess mutual affinity for each other and are ionized in the same solution plug, mass spectra often show molecular associates of varying degrees. The degree of association is controlled both by instrumental parameters and by the nature (functionalities, ionizabilities, affinities, *etc.*) of the molecules. By incorporating complementary molecules in favorable conditions, a multitude of information related to the formation of noncovalent complexes by these species during ESI-MS can be gathered. Work in our group currently focuses on two concerted approaches towards the study of supramolecular noncovalent structures in the gas phase by ESI-MS-based approaches (with liquid phase sample introduction).

One approach focuses on the formation and dissociation of metal-centered complexes. Such an approach has been exploited previously for various stereochemical and thermodynamic determinations based on the orientation and affinity of ligands about the metal center. Collision induced dissociation is used to distinguish between an analyte and reference channel where quantitative isomeric or chiral information can be exhibited. Scheme 1 details the popular approach, known most commonly as Cooks' Kinetic Method[2,3], used in this context. Our work focuses on the interaction of molecules containing guanidinium units. These functional moieties are known for their ability to exhibit both non-directed Coulombic interactions, as well as directed Hydrogen-bonding type interactions. We will show both isomeric and chiral discrimination based on analysis of guanidinium associates using the metal-centered-ordering approach[4].

Our second approach also concentrates on interaction of the guanidinium unit, but incorporates complementary functional units, such as anionic phosph[on]ates, sulf[on]ates, and carboxylates, rather than metal ions. ESI-MS is often performed in aqueous media, and thus the electrostatic interactions, such as exhibited by the above functional units, generate noncovalent complexes in high yield. The formation of these complexes can be monitored in the mass spectra. Their high yield also facilitates isolation and dissociation of each for elucidation of binding character. An extensive toolbox of qualitative and quantitative techniques exists to assess these interactions[1]. Results highlighting the differences in interaction offered by the various anionic units for guanidinium will be presented. The capability of the guanidinium for directional binding in this context will also be assessed. In addition, preliminary results highlighting the use of quinine-based chiral selectors complexed with peptide derivatives will be shown. For this system, information derived from the ESI-MS will be used to compare molecular recognition principles observed in the gas phase with those obtained in relevant liquid chromatographic separations[5].



Scheme 1. Detail of formation of and dissociation to metal-centered complexes. Kinetic discrimination is offered for analytes (A_x) by virtue of the interaction and arrangement of A_x with reference (Ref) about metal (M^{II}).

Taking separate approaches (metal- *vs.* non-metal-mediated) to the analysis of supramolecular complexes involving guanidinium-containing molecules grants us the ability to better characterize the interactive nature of this functional unit. General knowledge gained can be applied to the development of comprehensive screening techniques where molecular associations can be controlled to a high degree. Such an application would be beneficial in biopharmaceutical and drug development, where these functional groups are regularly encountered. Limitations that must be addressed are the influence of the ionization mechanism and the specific structural and spatial arrangement of the molecules in the associated complexes.

KS, CC, and WL gratefully acknowledge support for this research from the FWF (Austrian Science Fund, Grant #P15482), the CDL MRM (Christian Doppler Laboratory for Molecular Recognition Material), and the Austrian Academy of Sciences (DOC-Stipendium).

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DEVELOPMENT OF LUMINESCENT LANTHANIDE COMPLEXES: NEW APPROACH

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The great interest in studies of the luminescence properties of lanthanides is caused mainly by their prospective application in practice. But near IR 4f-luminescence of Yb(III) and Nd(III) ions (Fig. 1) is insufficiently applied, meanwhile it is known that this region is of special perspective for biomedical practice since the radiation of bio-objects is practically absent.

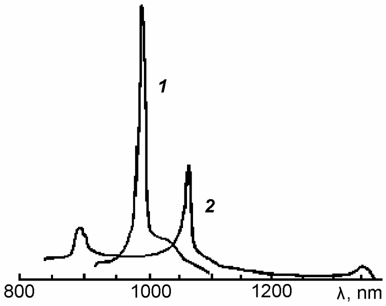

Fig.1. Luminescence spectra of Yb(III) (*1*) and Nd(III) (*2*) ions.

Now our research are focused on the investigations of near IR luminescence of Ln(III) in complexes with the following macrocyclic reagents: crown-esters, cryptands, cyclen derivatives and porphyrins1. In these systems, in contrast to the complexes with acyclic ligands, it is much better to minimize non-radiative losses of excitation energy. For 20 of these complexes the quantum yield and luminescence lifetime are the highest as compared to the known: φ - 1×10^{-2} and 2×10^{-3}, τ - 13 and 3 μs for Yb(III) and Nd(III), respectively. Nontrivial approaches to the increasing of the IR luminescence characteristics (in particular, with the use of heterometallic complexes), and perspectives concerning application of IR luminescence in biomedical practice are described and discussed as well.

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LANTHANIDE COMPLEXES WITH DIBENZO-SUBSTITUTED MACROCYCLIC LIGANDS

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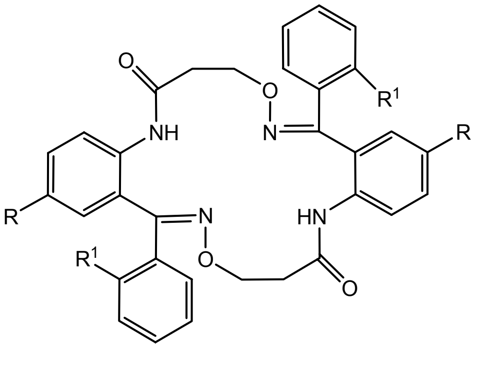
Lanthanide complex compounds have various biological activity with different organic ligands. Particularly some dibenzomacroheterocycles possessing definite anti-aggregative and psychotropic activity are especially interesting[1]. Spectral-luminescence properties of Eu(III), Tb(III) and Yb(III) ions in complexes with three 18-membered macrocyclic ligands (Fig.1) have been considered in given work.



R = CH_3, R^1 = H;
R = Br, R^1 = H;
R = Br, R^1 = Cl

Fig. 1. Structures of ligands.

The optimum conditions for the Ln-complex formation were examined. We have discussed the temperature, solvent and extra-ligand type, conformation factor impact on the processes of complex formation, their stability, spectroscopic characteristics. The changes in efficacy of the substituents in the macrocyclic structure are discussed.

The luminescence properties of lanthanide ions are discussed with the respect to the number of solvent molecules in the coordination sphere of the metal ion and to the mechanism of the ligand-to-metal energy transfer process.

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TWO PHOTON ABSORPTION ENGINEERING : FROM OPTICAL POWER LIMITING TO 3D MICRO-FABRICATION

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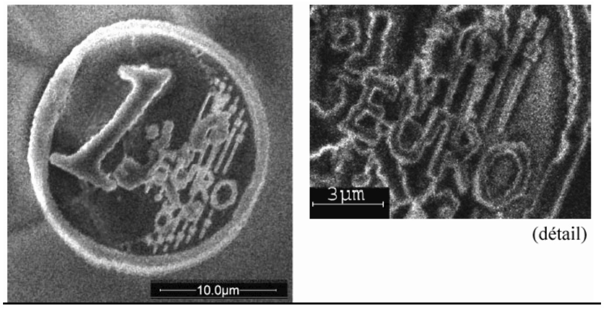
Two-photon absorption (TPA) in organic materials is a well-known process used in view of different applications for three-dimensional optical data storage[1], 3D-fluorescence imaging[2], photodynamic cancer therapy, optical limiting[3] and microfabrication[4]. This presentation concerns molecular engineering for the two last fields.

Coherent coupling of transition dipole moments between monomers were shown strongly to control physical properties of polyfluorene-based materials[5]. In that way, oligomers and dendrimers of fluorenes seem to be of great interest in the design of molecules with enhanced TPA cross-sections and efficient optical power limiting properties[6].

The TPA induced photopolymerization is a very promising method for the microfabrication of 3D structures and various micromachines[7]. This technique leads to highly resolved objects due to a large penetration depth of the incident beam and a tight confinement of the excitation volume around the focal point. New chromophores with a *D-Π-D* structure (*D* being an amino donor group and *Π* a weakly conjugated system) proved to be much more efficient than commercial UV initiators will be presented. They ensured radical formation under excitation in the initiation step and were successfully used for 3D microfabrication by using common and inexpensive lasers sources (0.5 ns pulses at 6.5 kHz repetition rate with a maximum pulse energy of 4 μJ at 532 nm). A example of structure obtained[8] (a "symbolic" one euro coin and a detail) is displayed Fig. 1.



(détail)

Fig. 1: a one euro coin of 20 μm diameter made by photopolymerization

For infrared, the selected photoinitiators present the general structure D-π-A-π-D in which A is an acceptor group with a molecule structure close to that of the Michler ketone (4,4'-bis(*N*,*N*-dimethylamino)benzophenone), a well-known UV photoinitiator; the molecule presented below (Fig. 2) was shown to be an efficient initiator for TPA photopolymerization in the IR range[9].

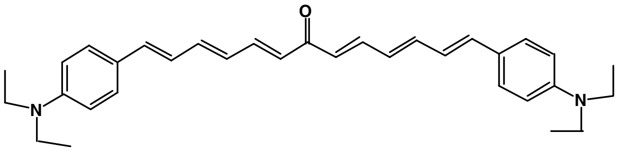


Fig. 2: Chemical structure of a TPA photoinitiator for polymerization at 1064 nm

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THERMODYNAMICS OF DNA-MINOR GROOVE RECOGNITION USING SOME OPTICAL AND CALORIMETRIC METHODS

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Structural pictures of drug-DNA complexes obtained by spectroscopy (in particular NMR) and crystallography represent rather impressive accomplishments, which teach us a great deal about how minor groove directed ligands bind to DNA. Unfortunately, such structural pictures, in general, tell us nothing about: (a) the stability of the complex in the solution (ΔG^o); (b) the thermodynamic nature of the overall molecular forces that drive complex formation in solution (ΔH^o vs. ΔS^o); (c) the temperature-dependent behavior of the complex (ΔH^o , Δc_P^o); and (d) the relative contributions that specific ligand-DNA interactions make to the binding affinity and specificity of the drug. Such assessments require thermodynamic characterizations of drug binding and drug-DNA complexes, preferably as a function of DNA sequence and drug structure. To obtain the relevant ΔG^o , ΔH^o , ΔS^o and Δc_P^o data one has to employ a combination of spectroscopic (UV, CD, fluorescence) and calorimetric (DSC, ICT) techniques.

In this light, we studied the mechanism of distamycin A (DST) and netropsin (NET) binding to the 17-mer duplexes D#1 and D#2: D#1 = d(GCAAGTTGCGATATACG) ·d(CGTATATCGCAACTTGC) and D#2 = d(GCAAGTTGC-GAAAAACG)·d(CGTTTTTCGCAACTTGC) .

It should be noted that D#1 contains 5'-AAGTT-3' and 5'-ATATA-3' sites that both favor dimeric (side by side) binding of DST molecules while in D#2 the 5'-ATATA-3' site is replaced by the 5'-AAAAA-3' site which at DST/5'-AAAAA-3' molar ratios lower than 1 prefers to accommodate only one DST molecule[1,2]. To follow binding and competition of DST and NET within the D#1 and D#2 minor grooves we employed spectropolarimetric (CD), spectrophotometric (UV) and isothermal calorimetric (ITC) titrations and the temperature dependent UV-spectroscopy. Model analysis was developed to describe binding of DST and NET within the measured duplexes. The resulting thermodynamic quantities of binding will be discussed in terms of different contributions due to solute-solute and solute-solvent interactions.

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KINETIC STUDY OF COMPLEXATION / DECOMPLEXATION OF MONOPHOSPHORUS ACID *DOTA* DERIVATIVE WITH COPPER(II) ION

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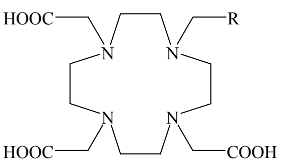
Bifunctional chelating agents (BFC) complexing copper(II) ion are utilized in nuclear medicine, *e.g.* in radioisotope diagnostics (^{64}Cu) or in tumor radiotherapy (^{67}Cu). BFC contain metal coordination unit (*e.g.* macrocycle) attached to biologically active molecules, *e.g.* monoclonal antibodies, small peptides, hormones, sugars, etc. The complexes should exhibit high thermodynamic stability and, of course, kinetic inertness under physiological conditions. Therefore, it is necessary to know thermodynamic and kinetic properties (formation and dissociation rate constants) of complexes of copper(II) and other biometal ion under experimental conditions similar to body fluids for applications *in vivo*.

In this work, the thermodynamic and kinetic properties of copper(II) complexes with macrocyclic ligands with phosphonic acid pendant arms (see the scheme) were studied.



R	
H	***DO3A***
COOH	***DOTA***
$CH_2P(O)(OH)_2$	***DO3AP***

The copper(II) complex of *DO3AP* ligand (log $\beta = 25.92$, $t = 25^{\circ}C$, $I = 0.1$ M) is much stable than respective complexes of *DOTA* (log $\beta = 22.25$) and *DO3A* (log $\beta = 21.65$). The protonation constants and molar absorptivities of protonated species $[Cu(H_nL)]^{(3-n)-}$ ($n = 1–3$) show that they are structurally different due to complexation of carboxylate/phosphonate group in axial position. The formation kinetics in copper(II)–*DO3AP* system ($t = 25^{\circ}C$, $I = 0.1$ M, pH = 1–7) was studied and it was found that rate of formation of copper(II) complex increase in order *DOTA* > *DO3AP* > *DO3A* > cyclen. In case of study of dissociation of copper(II) complex of *DO3AP* (t = 25–50 °C, $I = 5.0$ M $(Na,H)ClO_4$), the reaction mechanism was postulated and activation parameters were estimated. It can be concluded from results that rate of proton-assisted dissociation of copper(II) complex is comparable with rate of copper(II) complex of cyclen and, therefore, derivatization by the pendant arms on cyclen skeleton did not have any influence on its reactivity.

This work is supported by Grant Agency of the Czech Republic (203/02/0493 and 203/03/0168).

CHARACTERIZATION OF SELF-ORDERING NANOPORE DOMAINS OF ANODIC ALUMINUM OXIDE MEMBRANES

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One of the great challenges in nanotechnology is the fabrication and characterization of nanostructures in which the constituent units are highly ordered and regular. This is because a wide range of materials properties (magnetic, electronic, and optical) depends critically on the size, shape, and regularity of its substructure on the nanometer size scale. Anodic aluminum oxide (AAO), which is formed by the anodic oxidation of aluminum, has attracted much interest as a starting material for the fabrication of several kinds of functional devices with nanometer dimensions due to its naturally occurring nanometer-order channel array structure with a high aspect ratio [1,2].

For the improvement of the ordering of hole configuration of anodic alumina, two types of process have been developed; naturally occurring long-range ordering and ordering with ideally arranged hole configuration formed using anodization of prepattern aluminum [3-6].

In this work, two-step anodization process[7-8] utilized to grow the ordered aluminum oxides. The high pure aluminum (99.99%) plates were anodized in a 0.3 M oxalic acid electrolyte under anodic potential equal to 40 V. The ordering of nanopores, defined as ordered domains, has been characterized by using ex-situ scanning electron microscopy and contact mode-atomic force microscopy [9]. Based on the ex-situ SEM and AFM studies, the ordered domains show a typically linear growth behavior by increasing the duration of first anodization step as: $D = 0.55 \cdot t$, where D is the domain size in square micrometer and t is the first anodizing step time in hr.

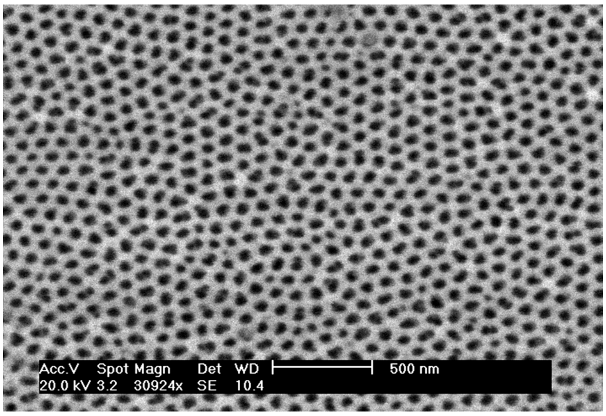

Fig. 1. SEM image of AAO membrane after anodizing for 1 hr and 45 min in the first and second steps, respectively

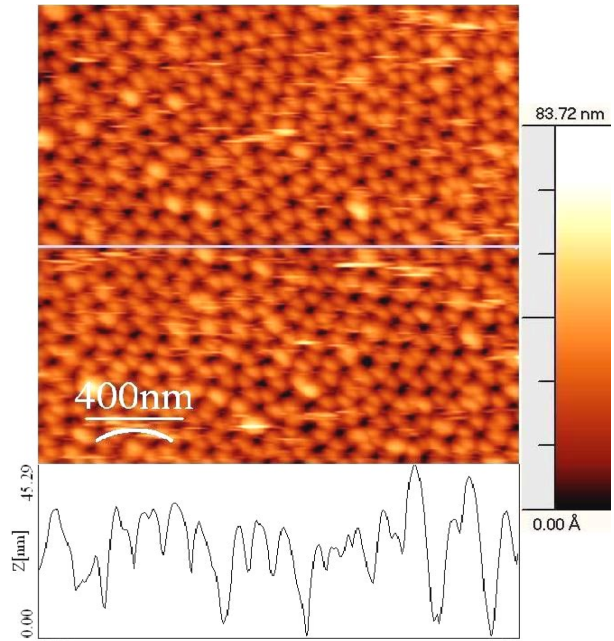

Fig. 2. AFM image from the top surface of AAO after anodizing for 6 h and 45 min in the first and second steps, respectively

Fig. 1 demonstrates SEM micrograph from the top surface of aluminum oxide, anodized for 1 hr and 45 min in the first and second steps of anodizing, respectively. However, ex-situ AFM image, shown in Fig. 2, illustrates the anodic aluminum oxide with increased domain size due to increased first anodizing step time up to 6 hr.

It is seen that an almost ideally arranged hexagonal cell configuration with a pore size of approximately 40 nm has been achieved. It can be found that the pore configurations contain many perfectly ordered domains, which are separated from the neighboring domains with different lattice orientations by grain boundaries and show polycrystalline structures. The size of the ordered domains depends linearly on the duration of first anodizing step.

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INTERFACIAL EFFECTS IN NANOLAYERS OF PORPHYRIN AND PHTHALOCYANINE DYES STUDIED BY SFM AND FT-IR SPECTROSCOPY FOR APPLICATION IN PHOTOVOLTAICS

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The paper deals with the study of the morphology of semiconducting (In_2O_3 and SnO_2) and metallic (Au) surfaces coated with the Langmuir-Blodgett[1] porphyrin, phthalocyanine[2] layers and with porphyrin-labelled "smart" polymers[2], which are good candidates as photoconverters in solar organic cells. Two techniques were used: scanning force microscopy (SFM) and absorbance-reflectance FT-IR spectroscopy. Interaction between dye layer and solid surface are discussed in a concept of organic photovoltaics.

In the experiments we follow the morphology of solid substrates and their changes upon deposition of dye and dye-polymer layers on the substrate surface. On the ground of the AFM the roughness parameter of the surfaces and its change upon molecular system deposition was estimated. It was shown that image of the surface morphology is closely connected with the relation between the magnitude of the substrate grains and the geometrical size of the dye systems. On the basis of the absorbance-reflectance FT-IR study the electron density redistribution at the dye-substrate interface was discussed[4].

The study of SFM image and IR of the solid surface coated with a dye layer is essential in understanding of some phenomenon occurring in photo-conversion in organic photovoltaics.

The Poznan University of Technology (grant BW 62-195/04) supported the paper. A.B. thanks the Foundation for Polish Science for a Fellowship for Young Scientists.

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ASSEMBLIES OF THE CROWN-CONTAINING DITOPIC RECEPTORS WITH ORGANIC MOLECULES

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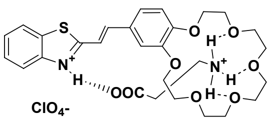
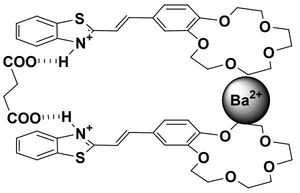
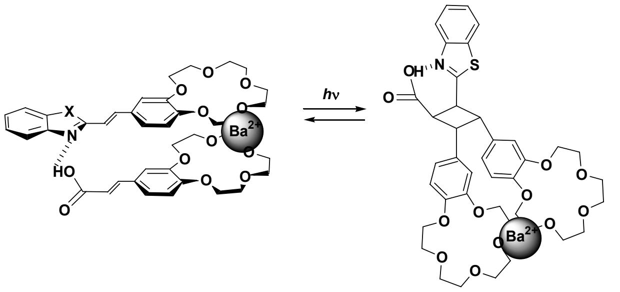
The construction of the synthetic molecules capable of recognizing and binding of small organic molecular substrates (ammonium salts, carboxylic acids) is important in the perspective that bioactive molecules such as amino acids, peptides and proteins containing amino and carbonyl groups can also associate with the same type of receptors. The recognition will result in the substantial change of the receptor characteristics what can be useful for biochemical analysis.

In the present investigation the assemblies of crown-containing hetarylphenylethenes with organic molecules were studied by UV and NMR spectroscopies and ESI-MASS spectrometric measurements. In designing of the receptors which able to form multicomponent molecular assemblies with ammonium cations, amino acids and dicarboxylic acids we used molecules possessing two binding centers of different nature. The main interactions involved in its recognition are hydrogen bonding, metal cation binding and steric complementary.







Aminoacids co-ordinate with heterocyclic residue and crown ether fragment to form the assemblies of different composition. The spectral characteristics and photochemical behavior of the assemblies are substantial differ from the initial crown-containing hetarylphenylethenes.

The study was supported by CRDF (Grant RC2-2344-MO-02), INTAS (Grant 2003-4696), RFBR (Projects No. 04-03-32677, 03-03-32849 and 02-03-33058), Program "Integration" of the Ministry for High Education of Russia.

SUPRAMOLECULAR COMPLEXES OF MODIFIED CYCLODEXTRINS WITH CROWN-CONTAINING HETARYLPHENYLETHENES: PHOTOCHEMICAL TRANSFORMATIONS AND INTERACTIONS WITH METAL CATIONS

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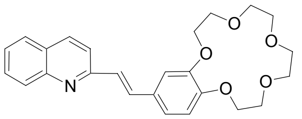
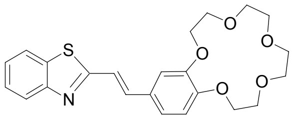
It is well-known that cyclodextrins (CDs), water-soluble, doughnut-shaped cyclic oligosaccharides consisting of six or more α-(1,4)-linked D-glucopyranose units, are able to form inclusion complexes (host–guest complexes) with a wide variety of guest organic molecules possessing suitable polarity and dimension characteristics. CDs have received a considerable attention, due to their ability to modify significantly physical and chemical properties of the included guests. For instance, an increase in the aqueous solubility of lipophilic compounds and an enhancement of the fluorescence emission of some molecules in the presence of CDs have been reported.

Crown-containing hetarylphenylethenes are novel macrocyclic ionophores, which are able to bind metal cations and possess easily recognizable changes in the absorption or fluorescence spectra of the sensor molecule. Such compounds are promising for the development of reagents for optical determination of metal cations and as components of photoswitching molecular devices. However, because of their hydrophobicity, crown-containing hetarylphenylethenes are poorly soluble in aqueous media, which constitutes an important problem for sensitivity of recognition.





In this study an electronic absorption and fluorescence spectrometric investigation of the host-guest interactions of CDs with crown-containing hetarylphenylethenes in aqueous media was carried out. The stoichiometry and thermodynamic characteristics of the inclusion complexes, including a temperature effect on the complex formation constant, were evaluated. A 1:1 and 1:2 stoichiometries were found for complexes of CDs with crown-containing hetarylphenylethenes. It was found the interaction with metal cations results in fluorescence quenching of supramolecular complexes. The photochemical behavior of supramolecular complexes includes *trans-cis* photoisomerization and electrocyclization reactions.

The study was supported by INTAS (Grant 2003-4696), RFBR (Projects No. 04-03-32677, 03-03-32849 and 02-03-33058), Program "Integration" of the Ministry for High Education of Russia.

REDUCTION OF MALEIC ACID IN AQUEOUS SOLUTIONS BY LOW VALENT COBALT COMPLEX

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Recently it was shown that a Ni(I) complex with tetraazamacrocyclic ligand reduces maleic acid. It was decided to investigate whether this is a general reaction of low valent transition metals. In the present study a Co(I) complex with maleic acid was investigated.

The complex $(\mathrm{Co^{I}L})^{+}$ (L=5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene) was produced by the pulse radiolysis technique from $(\mathrm{Co^{II}L})^{2+}$ and sodium formate in an aqueous phosphate buffer solution (0.1 mM, pH 6.0).

The $(\mathrm{Co^{I}L})^{+}$ complex reacts with maleic acid in a fast reaction. This reaction is followed by three consecutive reactions. The kinetics of all reactions were studied, product analysis performed and a plausible mechanism of the reaction is proposed.

CONSTRUCTION OF VARIABLE TEMPERATURE VISUAL READ OUT SYSTEM FOR SODIUM AND POTASSIUM IONS

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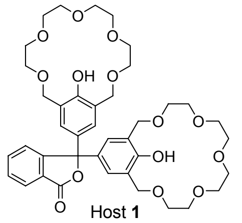
In living organisms, sodium and potassium ions play important and opposite roles in the maintenance of homeostasis. Studies of functional molecules having the ability to selectively capture metal cations were the dawn of host-guest chemistry or supramolecular chemistry[1]. Many chromogenic host molecules for sensing of metal cations have been reported[2]. However, to the best of our knowledge, there is no functional molecule that demonstrates opposite behavior toward two kinds of cation. We have reported that compound **1**, a hybrid molecule of phenolphthalein and two crownethers, was able to recognize various properties of guest molecules[3] by developing color. Herein, we report fascinating and opposite behavior toward sodium and potassium using host **1** accompanied by temperature change[4].

A variable temperature UV-vis spectrum of host **1** and sodium or potassium are shown in Fig. 1. The absorbance at around 566 nm by the complex of host **1** and NaOH increased as the temperature decreased (Fig. 1a). In contrast, color development between host **1** and KOH decreased as the temperature decreased (Fig. 1b). Since this observation was entirely unexpected and was the first example of sodium and potassium ions playing opposite roles in an artificial molecular recognition system, we further elucidated the mechanism.

First, we investigated the stoichiometry of complexation between host **1** and metal hydroxide analyzed by Job plots indicated that 1:3 host-guest colored complexes were generated in both cases of NaOH and KOH. Furthermore, variable temperature ^{1}H-NMR of host **1** and KOH, revealed the existence of complex having relatively high symmetry at low temperature. Thus, in both cases, the concentration of host-guest complex increased as the temperature fell. Furthermore, variable temperature IR spectra were measured. Therefore, in the presence of NaOH, the absorption corresponding to the carboxylate carbonyl group increased relative to the lactone carbonyl as the temperature decreased. The opposite behavior was observed between host **1** and KOH.

Based on the variable temperature UV, NMR, and IR spectra, we assumed that the different behaviors of host **1** with NaOH or KOH were caused by an equilibrium among the host molecule, the colored carboxylate complex and the colorless lactone complex (Fig. 2). As the temperature decreased, the colorled complex dominates in the case of host **1** and NaOH, whereas the colorless complex prevails in the case of host **1** and KOH.



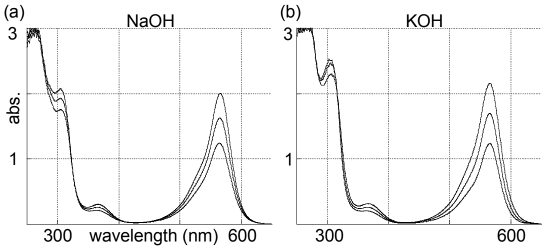


Fig. 1. (a) and (b) The variable-temperature UV-vis. spectra of host **1** with Metal-OH in methanol. [host **1**] = $2.8.10^{-4}$ M, [Metal-OH] = $1.0.10^{-3}$ M; (a) for NaOH, (b) for KOH

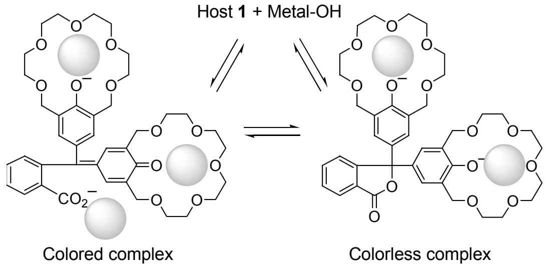


Fig. 2. Equiliblium among host **1**, colored and colorless complexes.

This work was supported by a Grant-in-Aid for Scientific Research (C) from the Japan Society for the Promotion of Science (JSPS).

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INTRAMOLECULAR ENERGY TRANSFER IN PYRENE-TETHERED RUTHENIUM(II)-POLYPYRIDINE COMPLEXES: TOWARD LONG-LIVED LUMINESCENT TRIPLET STATES

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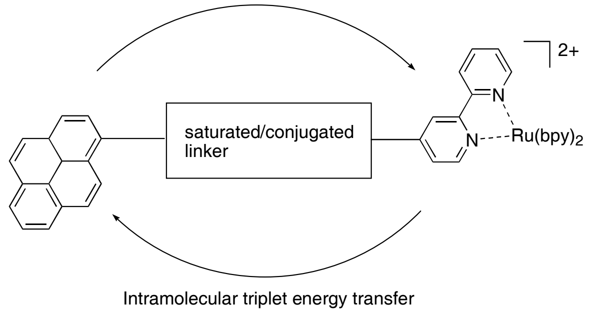
Chromophores that display long-lived luminescence are of prime interest for applications in emerging photonic technologies. In that respect, ruthenium(II)-polypyridine complexes represent versatile systems for the generation of oxygen sensors, luminescent labels, pressure-sensitive paints and electroluminescent materials. Recently we have shown that pyrene-containing ruthenium(II)-polypyridine complexes exhibited excited state lifetimes that greatly exceed those normaly observed in metal-to-ligand charge-transfer (MLCT) complexes[1-3]. This effect is due to the occurrence of reversible triplet energy tranfer between coexisting MLCT and intraligand (IL) triplet states. This presentation will focus on the synthesis and photophysical behavior in solution of pyrene-containing 2,2'-bipyridine ligands and their ruthenium(II) complexes. Particularly the combined influence of the pyrene chromophore and conjugated bridge will be discussed with regard to the occurrence of metal-to-ligand charge transfer (MLCT) excited states that display lifetimes well beyond those imposed by the energy gap law. Moreover the occurrence of IL and intraligand charge-transfer (ILCT) triplet states and their influence on the photophysical properties of supramolecular dyads will be described.



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RECOGNITION OF DIFFERENT SINGLESTRANDED AND DOUBLESTRANDED DNA / RNA SEQUENCES BY DIAZAPYRENIUM AND BIS-PHENANTHRIDINIUM DERIVATIVES IN AQUEOUS MEDIA

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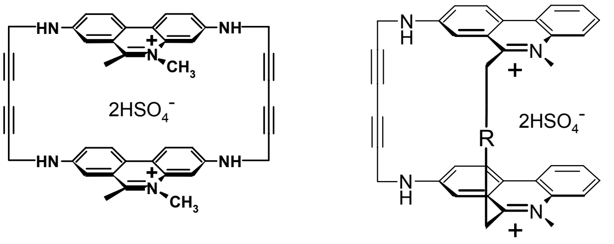
Among the number of small synthetic compounds that can bind to nucleic acids those with selective binding to single strand regions (hairpins, bulges) or to abasic sites of DNA or those that can selectively interact with single stranded (ss-) RNA sequences are rather rare[1]. They may be used for recognition and marking of single strand regions of DNA or RNA, or be used as selective RNA binders and hence potential antiviral agents. As shown for cyclobisacridinium derivatives, interactions with ss- and ds- DNA / RNA strongly depend on linker properties like length, position on aromatic moiety and possibility of additional interactions with polynucleotide[1,2].

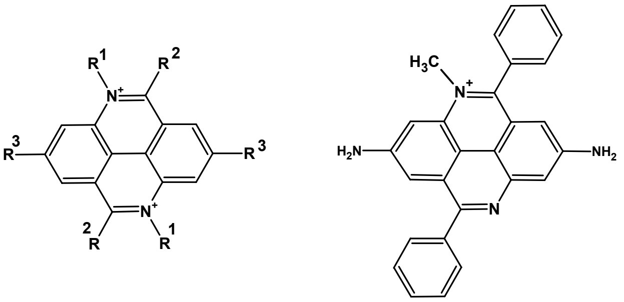
Different positioning of linkers in macrocyclic bis-phenanthridinium ligands (Fig. 1) type **I**[3] and **II**[4] efficiently controls their ss- over ds- polynucleotide affinity, former showing due to more stericaly restricted structure higher ss-polynucleotide selectivity.



I **II**

Fig. 1. Macrocyclic bis-phenanthridinium ligands.

A series of 4,9-diazapyrenium cations (Fig. 2, general structure **III**) proofed to be classical DNA / RNA intercalators[5], exhibiting also interesting anticancer activity[6].



III **IV**

Fig. 2. Studied 4,9-diazapyrenium cations.

However, derivative **IV** has shown striking difference in fluorescence response, namely for **IV** / poly GC complex 80% quenching and for **IV** / poly AU complex 100% fluorescence increase was observed. Also, **IV** formed unexpectedly stable complex with poly U at conditions close to saturation of polyU. All observed results lead to conclusion that **IV** binds to ds-polynucleotides by threading intercalation, additional interactions of strictly oriented amino groups of **IV** causing basepair dependent fluorescence changes. Same sterical restrictions cause selective interactions of **IV** with poly U inducing formation of the well organised, possibly helical structure of **IV** / poly U complex at saturation of binding sites.

Here presented examples clearly demonstrate importance of fine interplay between sterical rigidity and oriented interactions of substituents attached to intercalator moiety. On a base of shown results we plan design and synthesis of novel small organic molecules more selective toward different sequences of ss- or ds- polynucleotides.

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CONFORMATION AND π-CONJUGATION OF TETRAPHENYLPORPHYRINS WITH AN OLEFIN-BRIDGED SUBSTITUENT ON THE β-PYRROLE CARBON

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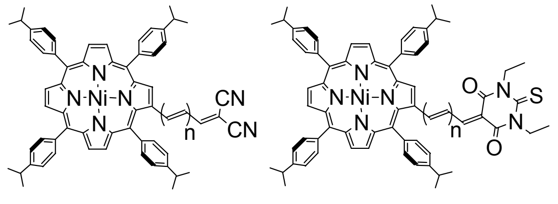
The conformation of tetraphenylporphyrin with appended electronic acceptor *via* olefin-bridge on the β-pyrrole carbon (Scheme 1) has been scrutinized experimentally and theoretically. Compelling evidence collected from UV-vis absorption and NOESY ^{1}H NMR experiment strongly suggest that coplanar or near coplanar conformation is highly possible between the olefin-linker and β-substituted porphyrin core in solution. In addition, the nonlinear optical (NLO) property, molecular first hyperpolarizability (β), of the porphyrins has been determined by electric-field induced second-harmonic (EFISH) technique. The active NLO property relies on the electronic coupling between the electronic acceptor and porphyrin, which is through π-conjugation and only conceivable with a coplanar or near coplanar conformation. The near coplanar conformation of the porphyrins has been further confirmed by INDO/1 Hamiltonian in the ZINDO computational calculations. The β-value of the porphyrins has been calculated using the time-dependent Hartree-Fock (TDHF) theory with the INDO/S Hamilonian and IS in general agreement with experimental results. The calculations also indicates there is intramolecular charge-transfer (ICT) characteristic in the Q as well as the B absorption bands of the porphyrins, supporting the π-conjugation of the molecules. INDO/S electron density calculation reveals that the range of ICT does not encompass the whole porphyrin core but mostly confines to the pyrrole ring attached with olefin-linked acceptor. This finding is consistent with the modest solvatochromic behavior and the medium NLO activity of the porphyrins compared with NLO chromophores with much fewer π-electron.



n = 0, **Ni(T*i*pPP)-0-CN**
n = 1, **Ni(T*i*pPP)-1-CN**
n = 2, **Ni(T*i*pPP)-2-CN**
n = 3, **Ni(T*i*pPP)-3-CN**

n =1, Ni(T*i*pPP)-1-TBA
n =3, Ni(T*i*pPP)-3-TBA

Scheme 1.

CONFORMATIONALLY FIXED PERYLENE BISIMIDE DYES: SYNTHESIS, FLUORESCENCE AND MOLECULAR RECOGNITION PROPERTIES

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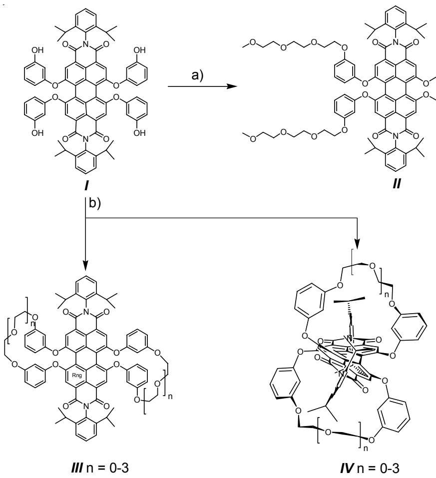
Bay-substituted perylene bisimides are a very important class of fluorophores due to their excellent optical properties, thermal and photochemical stability. Hierarchical self-assembly of perylene bisimides by metal-coordination or hydrogen-bonding leads to supramolecular structures like squares and polymers. The formation of highly ordered aggregates and liquid crystals by π-π-interaction facilitates applications in optoelectronic devices. These dyes exhibit an inherent axial chirality induced by the twisting of the π-system resulting from repulsive interactions of the substituents in the bay position[1].

We have synthesized macrocyclic perylene bisimides ***III*** and ***IV*** in order to investigate the influence of the conformation on the optical properties of bay-substituted perylene bisimides. In this contribution, we present UV-vis, steady-state and time-resolved fluorescence spectroscopic properties of dyes ***III*** and ***IV*** and conformation-dependent influences are figured out in comparison to the reference compound ***II***.



Scheme 1: a) $H_3C-(OCH_2CH_2)_3-O-p-Tos$, Cs_2CO_3, argon, 100°C, 23%, b) $p-Tos-O-CH_2CH_2O-(CH_2CH_2O)_n-p-Tos$ ($n = 0-3$), Cs_2CO_3, DMSO, argon, 100°C, 5 h

By using temperature-dependent ^1H-NMR spectroscopy, the inversion process arising from the axial chirality has been investigated for the ***IV*** series. The binding ability of these macrocycles will be subject of future investigations.

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NEW COORDINATION POLYMER NETWORK STRUCTURES BASED ON COPPER(II)-HEXAFLUOROACETYLACETONATE AND PYRIDINE CONTAINING BUILDING BLOCKS

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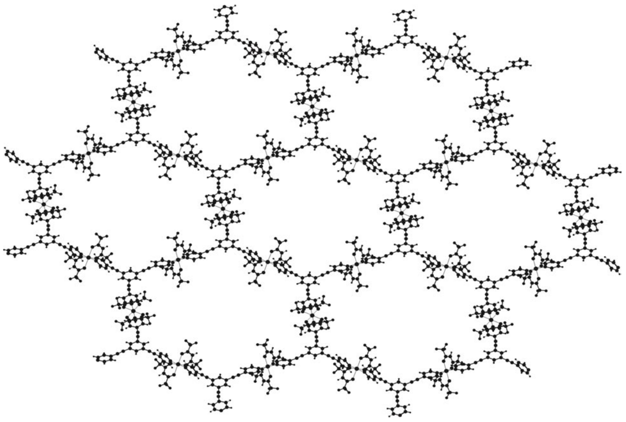
New coordination polymers composed of copper(II)hexafluoroacetylacetonate [$Cu(hfacac)_2$] and the trigonal or linear tectonic ligands 1,3,5-tris[2-(4-pyridyl)ethinyl]benzene (***1***) and 9,10-bis[2-(4-pyridyl)-ethinyl]-anthracene (***2***), respectively, are reported[1]. Preparation of the compounds is described, IR-spectroscopy and crystal structures are discussed, and potential sensor applications are shown.

The tectones ***1*** and ***2*** are prepared by Sonogashira cross coupling[2] of the bromo- and ethinyl-substituted components. Dependent on the geometry of the tectonic unit and the stoichiometric ratio of pyridine containing ligand to metal component [$Cu(hfacac)_2$] different coordination polymers are obtained, including 1D-zigzag, 2D-honeycomb or 2D-sheet structures (Scheme 1) that contain pores and cavities in the crystal with dimensions capable of organic molecule inclusion. Hence, a reversible sensor effect at the screening on a quartz micro balance (QMB) to volatile organic solvents is observed[3], suggesting potential use in chemical sensing.



Scheme 1. 2D-honeycomb structure of a coordination network.

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SYNTHESIS AND SELF-ASSEMBLY ON A GOLD SURFACE OF PHENYLPORPHYRIN DERIVATIVES

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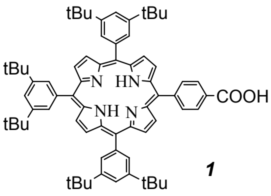
We reported the selective formation of supramolecular aggregates of cyanophenylporphyrins on a gold surface and showed that the shape and size of them were rationally controlled by tuning molecular structures[1]. In this paper, we present the synthesis and selective assemblies on a gold surface of carboxyphenylporphyrin ***1***, *t-bis*(carboxyphenyl)porphyrin ***2*** and *cis*-isomer ***3*** . These compounds were synthesized by Lindsey's method. The samples were sublimed and adsorbed on a Au(111) surface under UHV, and observed using scanning tunnering microscopy (STM).

Compound ***1*** formed dimers. *Trans*-carboxyphenyl compound ***2*** formed belt like structures which consisted of several straight molecular wires, and *cis*-isomer ***3*** formed tetramers and domains which consisted of *zig-zag* shaped molecular wires. These results show that the shape and size of supramolecular structures on the solid surfaces can be rationally controlled by tuning non-covalent interactions such as hydrogen-bonding between individual adsorbed molecules and molecule-substrate interactions.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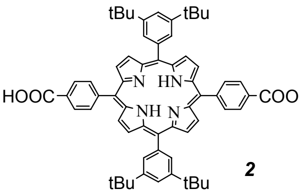
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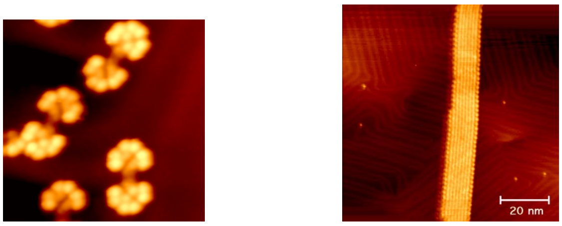

Fig. 1. STM images: left, compound ***1***; right, compound ***2***

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SYNTHESIS AND THERMAL BEHAVIOR OF BISFUNCTIONALIZED JANUS POLYESTER DENDRIMERS

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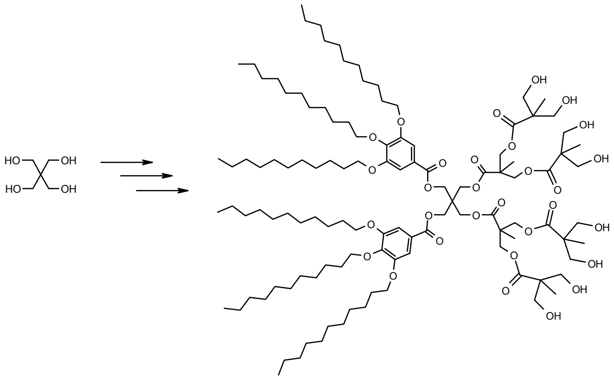
The growing demand for well-defined and functional materials in nanoscale supramolecular applications has lead to a huge increase in the development of synthetic procedures that combine architectural control[1] and incorporation of functional groups. As an answer of these demands, dendrimers themselves offer an appealing solution due to their unique properties[2].

Our modular synthetic strategy combines protection-deprotection sequence coupled with alternating divergent-convergent-divergent method for formation of the dendrimer generations and enables combination of two totally different functionalities into one dendrimer molecule. Particular interest was focused on the use of benzyl ether type monodendrons due to their known self-assembling properties[3,4]. Coupling these non-polar monodendrons with polar aliphatic arborol part creates a family of bisfunctionalized polyester dendrimers with possible self-assembling or when suitably modified, liquid crystalline properties. In presented work, the thermal behavior of JANUS dendrimers was characterized by the differential scanning calorimetry. The DSC results showed that all the hydroxyl terminated dendrimers of the first and some of the second generation, having substitution combinations of 3,4-, 3,5-, or 3,4,5 on aromatic sites, manifested at least single liquid-crystalline phase before melting. Whereas all the acetonide protected dendrimers exhibited merely melting transitions forming metastable phases on subsequent cooling and heating runs via crystallization or cold crystallization.



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MOVING TOWARDS DYNAMIC POLYMERS

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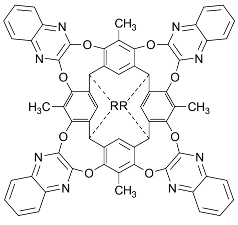
Supramolecular polymers are dynamic materials[1] that results from the association of monomeric species through noncovalent interactions; the reversibility of these self-assembled structures conveys many interesting properties, among which responsiveness to external stimuli is pivotal to the development of highly adaptive materials.

As a first approach to the synthesis of these kinds of materials, we will present the design, the preparation and the properties of cavitand **I**, capable of bimodal, independent self-assembling interactions, namely solvophobic aggregation and metal coordination[2]. For the first interaction the dimerization properties of a quinoxaline kite cavitand have been exploited: the driving forces for dimerization are dipole-dipole, Van der Waals and solvophobic interaction[3]. For metal complexation pyridine ligands have been introduced at the lower rim to dimerize through coordination to a metal center. This bimodal self-assembly protocol allowed the generation of a dual-coded dynamic supramolecular species, which has been transferred and amplified on surfaces.

The solvophobic interaction turned out to be not sufficiently strong to allow the formation of high molecular weight polymers in solution. To overcome this drawback in our self-assembly cycle, we have designed a new cavitand, the monomer **II**, bearing four phosphoryl groups at the upper rim in the inwards configuration. Cavitands equipped with four inward pointing PO groups at the upper rim have been reported to complex cationic guests with extremely high K_{ass}[4], large enough to lead to non-covalent polymer formation.



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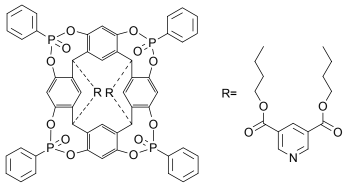

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PREPARATION OF COBALT *N*-CONFUSED PORPHYRIN AND ITS CHARACTERIZATION BY SPECTROSCOPIC AND ELECTROCHEMICAL TECHNIQUES

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A novel metallated *N*-confused porphyrin, Co(II) *N*-confused porphyrin (Co(II)NCTPP), was prepared. The new complex was characterized by UV-vis. spectroscopy in various solvents. It was shown that Lewis bases such as DMF and imidazole demetallate the complex. ESR spectroscopy confirmed the existence of a high spin (S=3/2) $3d^7$ Co(II) ion in the porphyrin. Cyclic voltammetry in CH_2Cl_2 showed a quasi-reversible wave with $E_{1/2}$ = 0.55 V *vs*. Ag/AgCl/KCl (satd.). Films of the Co(II)NCTPP on glassy carbon electrodes were stable in NaOH aqueous solutions and showed a reversible Co(III)/Co(II)NCTPP couple with $E_{1/2}$ = 0.025 V *vs*. Ag/AgCl/KCl (satd.) at pH 14.

INTERACTION OF TWO BIS-CROWN-ETHERS WITH ALKALI METAL IONS: AN ESI MS STUDY

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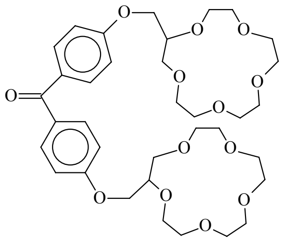
Generally, by the cooperative action of two adjacent crown-units, bis-crown-ethers tend to form stronger complexes with metal ions than the corresponding mono-crown ethers.

Novel, bis-crown-ethers (*1* and *2*) were synthesized. Electrospray ionisation mass spectrometry has been used to investigate the interactions in solution between bis-crown ethers (*1* and *2*) and Li^+, Na^+, K^+, Rb^+, and Cs^+ ions. The 1:1 complexes consist of *1* or *2* and the metal cations were observed. Moreover, the 2:1 and 1:2 complexes [bis-crown ether(s):metal cation(s)]were also observed.



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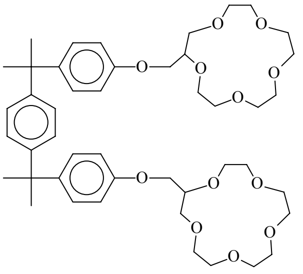

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CELLULAR - AND TISSUE DISTRIBUTION OF NEAR INFRARED PHOTOSENSITIZERS BASED ON CYCLOIMIDE DERIVATIVES OF BACTERIOCHLORIN

GEORGE V. SHARONOV[a,]*, TATYANA A. KARMAKOVA[b], ROEL KASSIES[c], ANNA D. PLJUTINSKAYA[b], MICHAEL A. GRIN[d], RAISA I. YAKUBOVSKAYA[b], ANDREY F. MIRONOV[d], MATTHIEU REFREGIERS[e], JEAN-CLAUDE MAURIZOT[e], PAUL VIGNY[e], CEES OTTO[c] and ALEXEI V. FEOFANOV[a]

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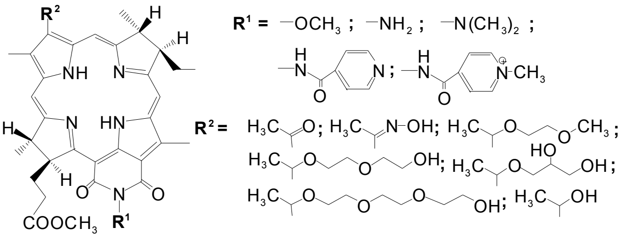
Various organic dyes absorbing in the near infrared (NIR) region were proposed as photosensitizers (PS) for photodynamic therapy of cancers. At the same time, the rational design of NIR PS is hampered for the lack of data on their intracellular and tissue distribution because of the absence of commercially available fluorescence NIR-microscopes. Here we report on the development of cycloimide derivatives of bacteriochlorin (CIBC, scheme), which have excellent photodynamic properties. We have created a sensitive NIR-confocal fluorescence NIR-microscopes and employed it as a unique tool that enabled a rational optimization of the CIBC structure through the study of the localization of CIBC in cells and tissue. We demonstrate that varying the structure of the substituents, a high intracellular concentration, controlled localization and, finally, improved activity of CIBC can be achieved. Our findings highlight the importance of CIBC structure optimization as a way of targeting PS to specific cellular organelles and improving its cellular accumulation and tumour selectivity.



This work was supported by INTAS-01-0461, PICS and RFBR (02-04-22001, 02-0448372) grants. G.V.S. was supported by a FEBS Summer Fellowship.

SUPRAMOLECULAR LOGIC GATES BASED ON TETRARUTHENATED PORPHYRIN FILMS

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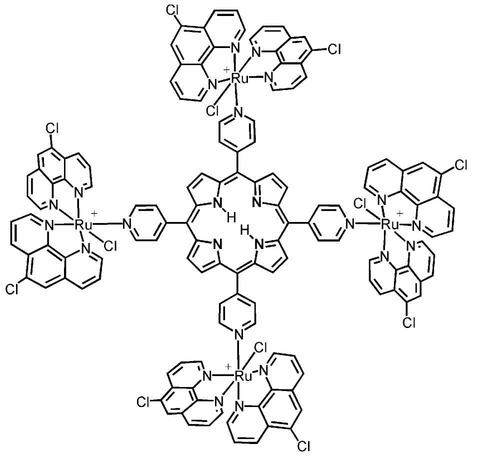
Supramolecular porphyrin and porphyrazine species containing suitable ancillary ruthenium polypyridine[1] or ruthenium clusters groups[2] form very homogeneous films by adsorption or electropolymerization, allowing also the assembly of organized multi-bilayers by dip-coating with suitable anionic sulphonated porphyrins and phtalocyanines. Such films exhibit electrical rectifying response, in addition to enhanced conductivity in the presence of reducing substrates, allowing applications as amperometric sensors for sulphite and nitrite, L-dopa and a number of drugs, such as acetaminophen[3]. In the presence of light, photoaction response has also been observed. Recently, their versatile electronic, optical and electrochemical properties have been successfully exploited for the development of photoelectrochemical devices[4].

Here we report on a simple device containing a supramolecular porphyrin film that can operate the three basic logic functions (AND, NOT, OR) and their combined forms. Our device consisted of two transparent ITO glass electrodes in a sandwhich arrangement with a micro laminar flow channel for the injection of the electrolyte solution containing the reducing species. One of the electrodes was modified by an electropolymerized molecular film[5] of a supramolecular porphyrin species (1) containing four [Ru(5-Clphenantroline)$_2$Cl]$^+$ coordinated to the *N*-pyridyl residues (Scheme 1).



Scheme 1. Structural representation of the supramolecular porphyrin species (1).

At 0.8 V, corresponding to the onset of the Ru(III)/(II) electrochemical wave, the film acts as a molecular switch, opening the gate for a sharp current increase in the presence of reducing species, such as nitrite[5] or ferrocyanide ions. However, in the presence of light, the supramolecular species are promoted to the excited state, and a photocurrent response is generated in the presence of mild oxidizing agents, such as ferricyanide or even dissolved dioxygen, as shown in Fig. 1.A. The photoaction behavior follows Butler's equation[6], decaying to zero as the applied potential approaches the flat band potential at 0.28 V. Therefore, by exchanging from 0.8 to 0 V, in the presence of light or in the dark, the system can be shifted from the electrocatalytical to the photoelectrocatalytical regime, providing the necessary conditions for activating the gates AND, NOT and OR, typical examples will be detailed.

In conclusion, by using the electrochemical potential, light excitation and the presence of chemical species such as nitrite or ferricyaned ions as inputs, and the resulting currents as outputs, multiple logic operations can be carried out with this system, allowing interesting applications in molecular electronics.

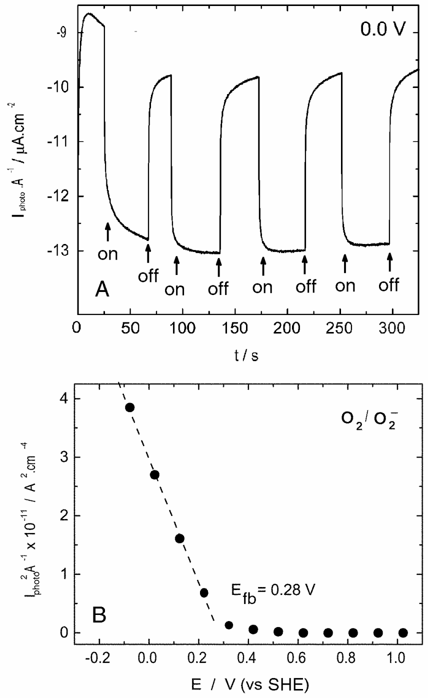


Fig. 1. Photoaction response of the supramolecular films of (1) in the presence of air, pH 4.5, bias potential = 0 V

Acknowledgements to FAPESP, CNPq, RENAMI and IM2C.

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SELF-ASSEMBLY OF IRON(II) AND RUTHENIUM(II) TERPYRIDYL METALLOMACROCYCLES

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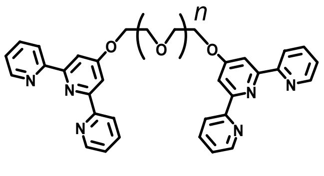
Ligands containing multiple bpy (bpy = 2,2'-bipyridine) or tpy (tpy = 2,2':6',2"-terpyridine) metal-binding domains have been extensively used in the metal-directed assembly of novel supermolecules such as helices, grids, catenanes and knots[1]. Metallomacrocycles can be formed through the interaction of six-coordinate metal ions with ligands containing two tpy domains[2-5]. Ligands ***1***, whose tpy motifs are linked through flexible spacer units, form metallomacrocyclic complexes on reaction with iron(II) salts. The metal:ligand stoichiometry in these cycles is dictated by the spacer length, with ligands containing short linkages (*n*=1) giving high nuclearity [3+3] and [4+4] cyclic species, and longer spacers (*n*=3-5) giving cycles of [2+2] or [1+1] stoichiometries. The formation of ruthenium(II) cycles from ligands such as ***1*** and the potential for forming mixed metal (Fe-Ru) metallomacrocycles using self-assembly methodologies will also be discussed.



1 (*n*=1-5)

We thank the University of Basel, the University of Western Australia and the Swiss National Science Foundation for support of this work.

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APPLICATION OF POLYACRYLIC ACID-BOUND MAGNETIC NANOPARTICLES IN THE TREATMENT OF DYESTUFF WASTWATER

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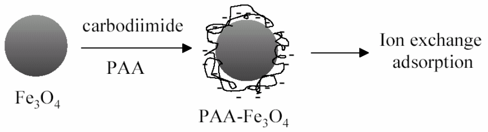
Polyacrylic acid (PAA)-bound Fe_3O_4 magnetic nanoparticles as a novel magnetic nano-adsorbent was developed (Scheme 1). Fe_3O_4 magnetic nanoparticles were prepared by co-precipitating Fe^{2+} and Fe^{3+} ions in an ammonia solution and treating under hydrothermal conditions. PAA was covalently bound onto magnetic nanoparticles via carbodiimide activation. The binding process did not significantly affect the size, structure, and superparamagnetic character of magnetic nanoparticles. The maximum weight ratio of PAA to Fe_3O_4 was 0.12 (*i.e.*, averagely two PAA molecules on a magnetic nanoparticle)[1].

Dyestuff wastwater may be carcinogens and toxic. Therefore, it is necessary to treat dyestuff wastwater prior to their discharge into the receiving water. Crystal violet is a cationic dye and also belongs to the group of triphenylmethane dyes. Some triphenylmethane dyes had been found to induce renal, hepatic, and lung tumor in mice[2]. Therefore, it is important to treat crystal violet in the environment. In this study, the magnetic nano-adsorbent was applied in the removal of crystal violet from an aqueous solution. It was shown that the magnetic nano-adsorbent not only could be manipulated magnetically but also exhibited quite high ion exchange capacity and fast adsorption and desorption rates for the removal of crystal violet due to high specific surface area and the absence of internal diffusion resistance. The adsorption and desorption equilibrium were usually achieved within 1-2 min, and the adsorption behaviors followed the Langmuir adsorption isotherms. Additionally, the reusability of magnetic nano-adsorbent and the effects of temperature and pH on the adsorption of crystal violet were also investigated. The developed magnetic nano-adsorbent will be useful in the removal of cationic dyes from dyestuff wastewater.



Scheme 1. Preparation of magnetic nano-adsorbent.

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DECAY LIFETIME OF *PARA*-SUBSTITUTED POLYSTYRENE IN SOLID FILMS AND IN DICHLOROMETHANE

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The fluorescence decay times of polystyrene, poly(4-bromostyrene), poly(4-chlorostyrene), poly(4-methylstyrene), poly(α-methylstyrene), poly(4-methoxystyrene), and poly(4-*tert* butylstyrene) were studied in solid films and in dichloromethane solution. A detailed analysis of the emission profile performed by nanosecond time resolved fluorescence spectroscopy confirmed the presence of monomeric polymer fluorescence as well as excimeric fluorescence in both media. The ratio of monomer to excimer contributions was found to be dependent upon the emission wavelength, but is not affected by polymer concentration. Both monomer and excimer fluorescence lifetimes as well as excimer intensity increase with increasing emission wavelength. An accompanying decrease in monomer contribution is also observed.

SPECTROSCOPIC STUDIES OF CHOSEN Ln(III) COMPLEXES WITH LIGNDS CONTAINING *N*-OXIDE GROUPS IN SOLUTION AND SOLID STATE

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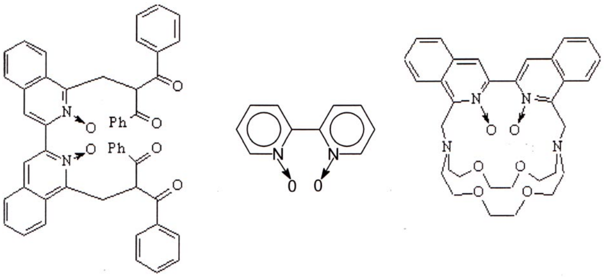
Photophysical characterization of chosen Ln(III) complexes, of general formulae ML and MLX, in solution and immobilized in xerogel matrix (prepared by sol-gel method), is presented. In these complexes the ligand L (Scheme 1) delivers energy from the ππ* ligand excited state to 4f excited states of the Eu(III) ion, while the ligand X (1,10-phenanthroline, 2,2-bipyridine, TPPO, phthalic and salicylic acid) plays a role of a coligand and expels additionally particles of the solvent (water or alcohol, effectively deactivating the excited state of this ion) from the inner sphere of the europium ion [1,2].



Scheme 1. The *N*-oxide ligands studied

Spectroscopic studies were made with use of absorption spectra of Nd(III) ions in the range of its hypersensitive transition ($^4I_{9/2}\rightarrow{}^2H_{9/2}$) which maximum and intensity are sensitive to the ligand field. Luminescence characterization of the EuL and EuLX compounds concerning their intensity, quantum yield, Φ, and luminescence lifetime, τ, of Eu(III) ion in solutions and solid are discussed. The luminescence intensities and lifetimes of Eu(III) ions were measured at room temperature and 77 K.

Obtained results indicate strong influence of absorption efficiency of the ligands, the type of coligands and matrices and the kind of the solvent, as well as temperature on the luminescence properties of the materials studied.

Good thermal properties and a photochemical stability of the solid compositions make them good candidates as potential luminescent materials in technical applications.

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SPECTROPHOTOMETRIC STUDY OF COMPLEX FORMATION BETWEEN LANTHANIDE (III) IONS AND WATER SOLUBLE PORPHYRIN IN METHANOL

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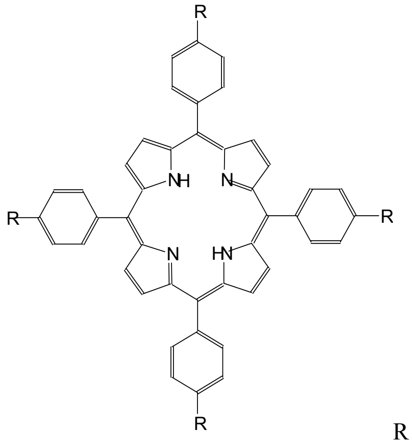
Porphyrins are versatile molecules whose physico-chemical properties can be easily adjusted by modifications of the electronic distribution on aromatic rings *via* peripheral substitution. A series of water-soluble porphyrins are derived from porphyrin precursor insoluble in water by introducing ionic groups such as $-COO^-$, SO_3^- or $=N-CH_3^+$. Chemistry of porphyrins and their metal complexes has been intensively studied because of their importance in biological systems[1-4].

The composition of porphyrin 4,4`,4``,4```-(porphine-5,10,15,20-tetrayl)-tetrakis(benzoic acid) (H_4L), have been subjected to spectroscopic study in the presence of lanthanide ions: La(III), Eu(III) and Yb(III).



R = COOH

The formation of complexes between the porphyrin and lanthanide ions has been studied and the values of their formation constants were calculated (log K = 3.7, 3.2 and 2.8 for La(III)-L, Eu(III)-L and Yb(III)-L, respectively). The stability constants of the studied complexes were determined by monitoring the changes of energy and intensity of Q bands of the porphyrin. Results of the spectrophotometric study have provided evidence proving the complexation of lanthanide cations by porphine in methanolic solutions mainly by peripheral carboxylic groups.

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MOLECULAR AND CRYSTAL STRUCTURES OF MESOGENICS BASED ON AROMATIC ESTERS

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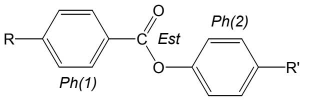
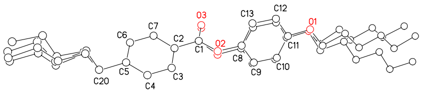
Molecular and crystal structure of ten mesogenics based on aromatic esters have been investigated at 120 K and 293 K:

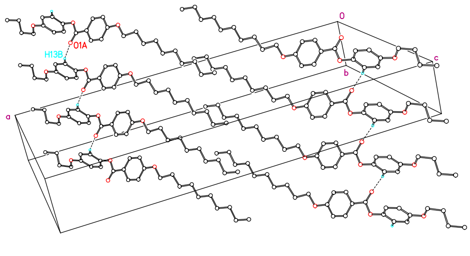


$R,R' = -(CH_2)_nCH_3, -O(CH_2)_nCH_3$

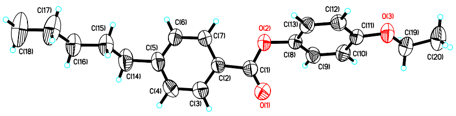
The *Ph(1)* and *Est* fragments are near coplanar, the *Ph(2)* fragment adopts any orientation depending on crystal packing requirements. The main peculiarity of the crystals is the occurrence of several (2, 3 and even 6) independent molecules with different conformations of the *Ph(2)*, R, R' groups in the unit cells:



Fragments of aliphatic groups are often disordered. The main common interest of the crystal packing is a separation of areas filled with aliphatic and aromatic fragments. In the aromatic arias, the *Ph(1)-Est-Ph(2*) moieties of the adjacent molecules are linked *via* weak interactions (stacking or *C*-H…π–system interaction, C-H…O hydrogen bonds). The aliphatic arias are very loosely packed.



The structure determinations at 293 K show that thermal ellipsoids of the aliphatic chains are increased in more extend than those of the benzene rings and have anisotropic pattern:



On the basis of these data, we may suppose that, when the nematic phase of these compounds forms on melting, the structure of the aromatic regions is partly retained due to the cooperative effect of weak interactions and thus they determine the anisotropic (liquid crystal) properties of the melts.

Acknowledgements, The Royal Society (2004 year), INTAS (03-51-4696).

STRUCTURE AND EXCITED STATE RELAXATION DYNAMICS FOR NANOSCALE MULTIPORPHYRIN SELF-ASSEMBLIES

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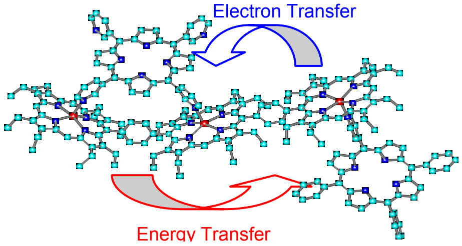
The important focus of our work is aimed at the formation and investigation of supramolecular nanoassemblies (based on tetrapyrrole compounds) showing vectorial electron transfer and enhanced light-harvesting efficiency for possible applications in the molecular electronics and nanotechnology. In this respect, using a combined covalent and non-covalent approach, we have developed a simple and yet potentially versatile strategy for fabricating self-assembled multiporphyrin arrays of controllable geometry and composition (up to 8 tetrapyrroles) *via* non-covalent binding interactions of the meso-phenyl bridged ZnOEP chemical dimers or trimers, $(ZnOEP)_2Ph$ or $(ZnOEP)_3Ph_2$, with di- and tetrapyridyl substituted tetrapyrrole extra-ligands[1, 2].



Using static, time-resolved fluorescent (experimental response $\Delta_{1/2} \approx 30$ ps) and pump-probe ($\Delta_{1/2} \approx 280$ fs) spectroscopy, the dynamics, pathways, mechanisms and competition between various non-radiative relaxation processes have been studied upon variation of redox and photophysical properties of interacting subunits as well the solvent polarity and temperature (77-295 K). The processes include: Foerster resonance energy transfer, photoinduced charge separation, bridge mediated long-range (r_{DA}=18-24 Å) superexchange photoinduced electron transfer, exchanged d-π effects.

The work was supported by Belarus National Program "Spectrum 05", Volkswagenstiftung (Ref: I/79435) and Belarus National Foundation for Basic Research (Grant Nr.Ph03MS-018).

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FLUORESCENCE CORRELATION SPECTROSCOPY OF SPERMINE-DNA INTERACTIONS – NANOSTRUCTURE AND PHYSICAL SUPRAMOLECULAR CHEMISTRY OF DNA CONDENSATION

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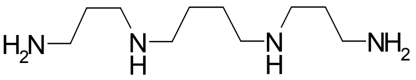
DNA condensation, one of the important events in life, enables lengthy polynucleotides to be stored as chromosomes in the nucleus of a cell, but utilising a minimum of space. This nanostructure can be achieved by the interactions of cationic lipids with the negative charges of DNA phosphate. Naturally occurring histones (lysine and arginine rich protein) and spermine help to maintain the folded conformations of DNA in cells. The use of spermine and its conjugates to compact DNA by condensation has been recently studied[1-5], with an aim to use self-assembled DNA nanoparticles in gene therapy. The condensed DNA particles are in the range 10-180 nm, typically 50-150 nm in outer diameter. This DNA compaction facilitates several key aspects of self assembly: its stability in extracellular compartments, cellular uptake, and other intracellular processes such as nuclear entry.



Spermine

DNA intercalating agents have been widely used to determine the polycation-DNA interaction. *e.g.* ethidium bromide (EthBr), propidium iodide, PicoGreen. EthBr steady state fluorescence assay is the mostly used simple technique to monitor the conformation change of DNA over the condensation process[3]. EthBr, intercalated in stacks of DNA base pairs, fluoresces at 600 nm by direct excitation at 546 nm, or more efficiently through energy transfer from DNA base by excitation[4] at 260 nm. On DNA condensation at increasing ammonium/phosphate (N/P) charge ratio, a decrease in EthBr fluorescence intensity was measured. Spermine-mediated DNA condensation occurred at N/P charge ratios ranging from 0.25 to 3.00. In addition to these fluorescence techniques, the formation of nanoparticles by DNA condensation can be observed in a light scattering (LS) assay, measuring UV apparent absorption at $\lambda > 300$ nm. DNA complexes were formed at N/P charge ratios ranging from 0.50 to 3.00. The optimal N/P charge ratio for both EthBr and LS assays was 3.0[5].

Fluorescence correlation spectroscopy (FCS) is a technique where fluctuations in the detected fluorescence from small molecules (such as DNA intercalating probes) are used to study dynamic processes on the molecular scale. We have demonstrated for the first time that FCS is able to monitor the condensation process of DNA-plasmids on a single molecule level[6-8]. DNA plasmids are loaded with fluorescent dyes: ethidium bromide, propidium iodide, or PicoGreen and the diffusion coefficient of single plasmids are determined by FCS. Condensation induced by positively charged condensing agents like *e.g.* spermine leads to a dramatic increase in the diffusion coefficient. The advantages of the FCS approach in comparison to standard fluorescence techniques are: a) use of lower dye concentration, b) information of possible plasmid sub-populations, c) the possibility to monitor the condensation process on a single molecule level.

Considering the success in using FCS, more fluorescence techniques have been developed from FCS *e.g.* in vivo FCS, fluorescence resonance energy transfer (FRET) by FCS. These would reveal more detailed nanostructure and physical chemistry of DNA condensation. Ultimately a better understanding of DNA condensation will lead to the development of more efficient DNA condensing agents. Designed small molecule fluorescent probes will play an important part in this[2,5].

We thank Universities U.K. for an ORS award to N.A.

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MOLECULAR MODELLING OF DNA-ETHIDIUM BROMIDE-POLYAMINE WEAK INTERACTIONS – DNA BENDING AND CONDENSATION LEADING TO SELF-ASSEMBLY OF A NANOPHARMACEUTICAL

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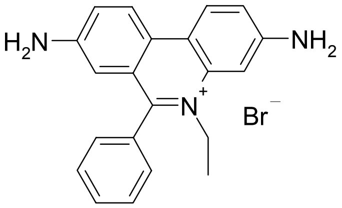
Polyamines and their conjugates electrostatically interact with DNA to form self-assembled nanoparticles[1]. Spermidine, a tri-amine, was first reported to condense DNA[2]. The DNA collapse was explained by the counterion condensation theory further developed by Manning[3]. Naturally occurring and biologically useful polycations (such as the tetra-amine spermine and spermidine) were found to lower the energy of transition for DNA nanoparticle self-assembly[4]. From structure-activity relationships (SAR) within naturally occurring and synthetic polyamines, the importance of positive charge distribution in DNA condensation efficacy has been highlighted[1]. In addition to this polyamine SAR, DNA bending (conformational change) seems to exhibit selectivity for certain base sequences. Toroidal DNA particles were formed in which the DNA is organized within a series of equally sized contiguous loops that precess about the toroid axis[5-9]. The size of the nucleation loop has a direct effect on the diameter of the formed toroid, whereas solution conditions govern toroid thickness[5-9].



Ethidium bromide

Ethidium bromide (EthBr) intercalates between base pairs of DNA and fluoresces at 600 nm when excited (indirectly through the DNA bases) at 260 nm or at 546 nm (direct excitation of EthBr). Upon changes to the DNA conformation, the fluorescence is decreased due to a complex mechanism for the loss of EthBr intercalation binding sites. Thus, EthBr has been widely used in DNA-polyamine interaction studies including polyamine vector-based gene therapy. The fluorescence assay was performed by titrating polyamine against DNA to achieve different interactions. In addition to these fluorescence techniques, the formation of nanoparticles by DNA condensation was also confirmed by a light (320 nm) scattering assay[10].

Computer modelling of bent DNA containing intercalated ethidium was performed to obtain theoretical data to complement the above experimental results. Bent DNA was constructed using a newly designed algorithm, NASDAC (Nucleic Acids: Structure, Dynamics, and Conformation), using an algorithm for the computation of 2'-deoxyribose-phosphodiester backbone conformations that are stereochemically compatible with a given arrangement of nucleic acid bases along a DNA structure. The algorithm involves the sequential computation of 2'-deoxyribose and phosphodiester conformers beginning at the 5'-end of a DNA strand. Regardless of the conformational complexity of these structures, we are able to compute backbone conformations for each structure. Hence the algorithm, which is currently implemented within the new computer program NASDAC, should have generally applicability to the computation of DNA structures[11]. Intercalation sites based on X-ray data were included at regular intervals in the duplex, and ethidium was docked into these sites. The duplex was progressively bent in a systematic manner, and the affinity of ethidium for each bent duplex was calculated. The results provide a basis for the interpretation of the fluorescence quenching data, and the modelling provides insights into the mechanisms of DNA bending as found in the bending by polyamines and especially by lipopolyamines leading to the self-assembly of nanoparticles.

We thank Universities U.K. for an ORS award to N.A.

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SYNTHESIS AND BIOLOGICAL TESTING OF LIPOPOLYAMINE N^2,N^3-DIOLEOYLSPERMINE – SELF-ASSEMBLY OF A NANOPHARMACEUTICAL FOR PLASMID DELIVERY

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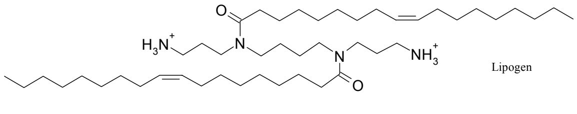
Spermine is a natural tetra-cation polyamine which plays important roles in DNA condensation, and especially (together with histones, naturally occurring polymers of lysine and arginine) in maintaining the folded conformations of DNA in the nucleus. We are designing novel small molecule DNA-condensing agents, modified synthetic polyamine-conjugates (lipopolyamines), using spermine as the polyammonium ion moieties conjugated with lipophilic groups (such as steroids *e.g.* cholesterol, bile acids, long alkyl or alkenyl chains *e.g.* C_{18} fatty acids), as part of a programme to develop more efficient non-viral gene delivery systems in order to improve DNA uptake by target cells for safe and effective non-viral gene therapy (NVGT). Non-viral vector mediated cell transfection remains a poorly understood phenomenon both *in vitro* and *in vivo*, but it is inherently safer and can transport a significantly larger DNA payload than using a viral vector[1].

N^2,N^3-Dioleoylspermine (LipoGen) is a lipospermine with two oleoyl chains acylating both secondary amines. This simple, small molecule combines the characteristics of both a cationic lipid and a fusogenic (lipid bilayer disrupting) lipid, such as dioleoyl phosphatidylethanolamine (DOPE), in its structure. Protection of amino groups is crucial to efficient synthetic control of polyamines[2,3]. Trifluoroacetylation with ethyl trifluoroacetate (2.0 eq) was successfully used to protect only the primary amino functional groups in spermine (1.0 eq)[2-4]. N^1,N^4-Trifluoroacetylspermine was reacted with oleic acid (2.2 eq) to form N^2,N^3-dioleoylspermine using 1,3-dicyclohexylcarbodiimide (DCC) (2.4 eq) and catalyzed by 1-hydroxybenzotriazole (HOBt) (1.0 eq). The removal of this protecting group was easily carried out at alkaline pH (11.0). Given N^2,N^3-dioleoylspermine carries two positive charges at neutral pH, the removal of unreacted starting materials and by-products (*e.g.* oleic acid, dicyclohexylurea etc) was carried out by column chromatographic elution over flash silica gel with DCM/MeOH (5/2 v/v) as mobile phase. Then, N^2,N^3-dioleoylspermine was collected by elution with DCM/MeOH/NH_4OH (25/10/1 v/v/v). The obtained sample was pre-column derivatized with dansyl chloride and its homogeneity analysed by HPLC with fluorescence detection[5,6]; full spectroscopic identification was carried out by using NMR and MS.

DNA-bending experiments were monitored by UV-fluorescence spectroscopic techniques to analyse and quantify the efficiency of DNA condensation. This condensation was achieved by DNA phosphate charge neutralisation with cationic lipopolyamines. The ammonium ions interact with and then condense DNA, so we study the formulation and analytical chemistry of these polyamine conjugates acting as histone mimics. DNA condensation, the first step in gene delivery, was studied by the fluorescence quenching of ethidium bromide (EthBr) to monitor the formation of nanoparticles[7]. The fluorescence yield of EthBr (λ_{ex} = 260 nm,

λ_{em} = 600 nm) increased on intercalation between adjacent base-pairs, and then gradually decreased when the DNA phosphate anions were neutralised by increasing the ammonium/phosphate (N/P) charge ratio. We showed that lipophilic modification of spermine resulted in a more efficient Enhanced Green Fluorescent Protein (pEGFP) cDNA condensation (15% residual fluorescence, in the EthBr assay, at N/P charge ratio 2.5) compared to tetracationic spermine (50% at N/P charge ratio 3.0). Particle formation was confirmed by measuring UV light scattering (LS)[8], recorded as increased absorption at λ = 320 nm. This is compared to the efficiency of cell line transfection with plasmid DNA encoding EGFP, and condensed by the same lipopolyamine. The transfection efficiency (62% at optimal charge ratio 2.5) is significantly higher than in the control cells transfected with cationic lipid (DOTMA/DOPE) (10-40%). Given the superiority of this novel lipopolyamine (to spermine), we are studying its mechanisms and kinetics in NVGT.



Lipogen

We thank Universities U.K. for an ORS award to N.A.

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DESIGN AND SUPPORTED SYNTHESIS OF FERROCENE MODIFIED OLIGONUCLEOTIDES FOR ELECTROCHEMICAL DETECTION OF DNA HYBDRIDIZATION REACTION

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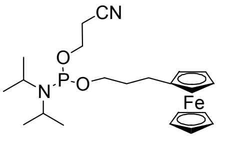

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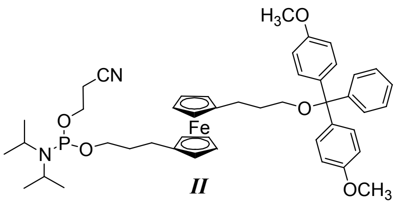

II

During the last years, extensive research has been directed towards the detection of specific nucleic acid target sequence using real-time methods for applications in clinical diagnostics, environmental protection or food quality control. In that context electrochemically-based sensors show great promise due to their high sensitivity, low production cost and compatibility to make small devices. Detection strategies are based on the change in the electrochemical response of a label grafted onto oligonucleotide probes. Ferrocene as label has been the subject of intense investigation due to its good stability and easy synthetic chemistry.

To limit the occurrence of side reactions and to reduce the number of purification steps we describe a new approach toward ferrocene-labeled ODNs in which the ferrocenes unit ***I*** or/and ***II*** are directly incorporated during automated DNA synthesis[1].

The synthesis of a new class of ferrocene derivatives will be reported. The electrochemical and hybridization properties of news ferrocene-labeled ODNs will be discussed[2].

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COMPLEX FORMATION OF METALLACROWNS WITH LANTHANIDE(III) IONS

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Metallacrowns are a new class of macrocyclic compounds, where the metal is an integral part of the macrocycle ring[1]. These macrocycles have structural similarities with the crown ethers but show a larger structural and chemical variety because the hydroxamic acid, the ring metal and the central metal can be varied. The building block of a metallacrown is a hydroxamic acid. A hydroxamic acid contains the functional group C(O)NHOH. Metallacrowns can be synthesized in two steps, the first step involving the synthesis of the ligand and the second the self-assembly of the ligand in presence of the metal ions. Varieties of complexes with copper(II) as ring metal and lanthanide(III) ions as cavity ions have been synthesized. Characterization methods include mass spectrometry (MS), nuclear magnetic resonance (NMR) and X-ray diffraction.

A first class of ligand we used are hydroxamic acids derived from alpha amino acids. Because alpha amino hydroxamic acids (except glycine hydroxamic acid) are chiral, the resulting metallacrowns will also be chiral. Circular dichroism (CD) was used to study these metallacrowns. A second class of metallacrowns with derivatives of lactic hydroxamic acid are currently also under investigation although they have not been isolated yet.

The lanthanide(III) ion in a 15-metallacrown-5 is coordinated by five oxygen atoms from the ring. Because lanthanide(III) ions have a high coordination number, oxygen atoms of additional ligands as nitrate or water molecules can also coordinate them. These water molecules play an important role in the relaxation efficiency of the metallacrown. Compounds that show good relaxation are used in medicine as contrast-agents (CA) for magnetic resonance imaging (MRI)[2].

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LANTHANIDE(III)QUINOLINATES, A NEW INSIGHT IN "OLD" CHEMISTRY

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Quinolines are usually known as a ligands for the gravimetric analysis of lanthanide(III)ions. Pirtea mentioned this for the first time in 1937[1]. Further research focused on thermal behaviour, infrared spectroscopy and behaviour in solution. Recently the quinolinates with erbium, neodymium and ytterbium came to interest because of their infrared luminescence[2].

The literature concerning these types of complexes often shows no or a very limited structural analysis. The structure is assumed to be $Ln(C_9H_6NO)_3$, although some authors doubt this[3].

We tried to fill this gap by examining these compounds with NMR, ESI mass spectroscopy and CHN analysis. It became quite clear that the literature methods don't give products matching tris coordination. We found that the product consists of a mixture of compounds depending on the structure of the ligand used.

This research was made possible by the European Community under contract GROWTH No: GRD2-2000-30346 OPAMD, the K.U.Leuven (GOA 03/03) and the Institution for the Promotion of Innovation by Science and Technology in Flanders (IWT).

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THE INVESTIGATIONS OF LANTHANUM MICROAMOUNT'S BEGAVIOR IN CHEMICAL PROCESSES

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The chemical behavior of micro-amount of ^{142}La in some physico-chemical processes is of certain scientific interest. For example in sorption processes. ^{142}La – isotopes were obtained as a product of fission reaction of ^{235}U (ref. [1]). ^{142}La – isotopes were accumulated in distilled and mineral water, HCl, KOH, Citric acid, Acetate acid, Ethanol and some other solutions. The concentration of ^{142}La was $\approx 10^{-14}$ mol/l.

Sorptions of ^{142}La by inorganic sorbent (Titanium Phosphate) was studied using a sorption column 60-70 mm high and 5 mm in diameter. The sorbent mass being 600 mg, the solution feed rate 2,5 ml/min. The content of the ^{142}La was determined from their characteristic γ-radiation. The investigations of ^{142}La sorption in different conditions as well as the information about structure of sorbent's surface allowed to make some conclusions about mechanism of sorption processes and about behavior of ^{142}La micro amounts[2].

Table 1. The sorption coefficients of ^{142}La by Titanium Phosphate from different solutions.

Solution	Sorption coefficients
HCl water solution	0,54 ±0,07
KOH water solution	0,12± 0,05
Acetate acid water solution	0,45± 0,021
Citric acid water solution	0,0 ±0.04
Ethanol 42%-water solution	0.57± 0,09

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SPIN TRANSITION OF IRON (II) COMPLEXEX IN 2D AND 3D FRAMEWORKS USING X-RAY ABSORPTION STUDIES.

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Spin crossover phenomenon is often observed in most of Fe(II) complexes with ligand field strength in the appropriate range. The spin transition of Fe(II) in an octahedral coordination is between a paramagnetic quintet $^5T_2$ (S=2, $t_{2g}^4e_g^2$) and a diamagnetic singlet $^1A_1$ (S=0, t_{2g}^6) state. Such transition can be induced by varying the temperature, the pressure or through photo-excitation/relaxation.

A 2D spin crossover system with $Fe(NCS)_2$ building blocks bridged by a bifunctional ligand, 4,4'-bis-1,2,4-triazole (btr), to form $[Fe(btr)_2(NCS)_2]$ layered framework[1], crystalized in C 2/c space group, which shows a cooperative spin crossover centered at 130 K with a hysteresis of 20 K.

The 3D framework can be further obtained by replacing the *trans*-NCS ligands with additional bridging ligand of btr to form $[Fe(btr)_3]$ $(ClO_4)_2$ (ref.[2]). The cation of $[Fe(btr)_3]$ is actually a supramolecule with Fe at the corner and btr ligand at the edge, forming a 3D porous framework where the anions, ClO_4^-, are located inside the pore. It crystalized in R-3 space group.

This material shows a two-step spin crossover, an abrupt one at 188 K and a gradual one from 210 K to 250 K due to two different sites of Fe(II) in the framework. The spin transitions of these 2D and 3D framework systems are monitored by X-ray absorption spectroscopy and the magnetic measurements. The crystal structures and the possible mechanism of the spin transition will be discussed.

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SUPRAMOLECULAR NITRENE CHEMISTRY: PHOTOLYSIS OF THE FERROCENYL AZIDE@ß-CYCLODEXTRIN COMPLEX

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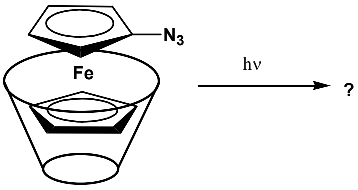
Takahashi[1] found that ß- and γ-cyclodextrin (CD) form a 1:1 whereas α-CD forms a 2:1 complex. The proposed orientation of ferrocene inside the CD based on circular dichroism, and ^1H NMR, UV, IR spectroscopic properties, and thermogravimetric analysis were reported[2]. Mössbauer spectroscopic studies on molecular rotation and lattice dynamics[3], the X-ray structure[4] and 2D NMR[5], and molecular mechanics calculations[6] of the FcH@CD complexes are described in the literature as well. The photolysis and thermolysis of ferrocenyl azide in organic solvents has already been described[7].

Among the reactive species, supramolecular carbene chemistry has only been explored in recent years. However, until now there are no reports in the literature about supramolecular nitrene chemistry.

Therefore, we decided to photolyse the 1:1 ferrocenyl azide[7] ß-CD complex. We will present structural and mechanistic aspects of its reactions on the poster (Fig. 1).



Fc-N_3@β-CD

Fig. 1. Photolysis of the 1:1 azidoferrocene ß-cyclodextrin inclusion complex.

We thank the Fonds zur Förderung der wissenschaftlichen Forschung in Österreich (Project P12533-CHE) for financial support.

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VESICLES FORMED BY NON-PHOSPHOLIPID SELF-ASSEMBLY

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Lipids are naturally occurring nanotechnology building blocks. Since the applicability of natural phospholipids is limited due to several factors, such as low stability against oxidation and biodegradation, there is a growing interest in synthetic mimics of phospholipids that can be used as building elements of lipid self-assembled structures.

Lactylated monoacylesters of propylene glycol (LMP) is a nonionic non-phospholipid that is mainly used as an emulsifier in processed foods. The headgroup contains polymerized lactic acid units. Due to its low polarity, LMP might be exploited to tune the interface characteristics in lipid mixtures.

By using differential scanning calorimetry and small- and wide-angle X-ray diffraction techniques, we ascertained that LMP packs into a number of polymorphic crystalline phases depending on the temperature, forming a stable α-crystalline phase between 9 and 40 °C, which melts into an isotropic liquid phase.

In order to assess the potential of LMP for the formation of hydrated lipid mesophases, binary lipid mixtures were assembled in excess water by the addition of positively and negatively charged colipids of different geometrical shapes, such as dihexadecyl phosphate, dihexadecyldimethylammonium bromide (DHDAB) and didodecyldimethylammonium bromide. Full miscibility was only detected for LMP and DHDAB. We could prove the self-assembly into vesicular structures with a membrane thickness of 5.1 nm for the LMP/DHDAB mixture at a ratio of 60/40 (w/w).

Supported by the European Commission (Marie Curie Industry Host Fellowship, HPMI-GH-01-00116-01).

COUMARIN-BASED NOVEL REVERSIBLE THERMOCHROMIC MATERIALS

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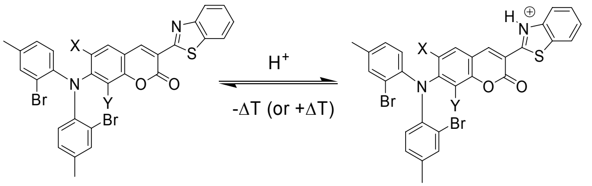

3Br-1: X = Br, Y = H,
3Br-2: X = H, Y = Br

3Br-1· H$^+$: X = Br, Y = H,
3Br-2. H$^+$: X = H, Y = Br,

Fig. 1. Reversible protonation of **3Br-1** and **3Br-2** promoted by cooling or heating

Our research aim is to design coumarin 6-based reversible chromic materials. Bulky *ortho*-substituted aryl groups are implanted in lieu of ethyl groups of coumarin 6 to create non-planarity around amino center, and thus result in shortening the effective conjugation length to the protonated site of benzothiazole, narrowing the energy gap between the neutral and protonated forms and rendering the color reversibility possible. Accordingly, two rather sterically bulky *ortho*-brominated arylgroups (**3Br-1** and **3Br-2)** were built around nitrogen atom to proof the concept.

Reversible thermochromic behaviors of **3Br-1** and **3Br-2** were characterized by variable-temperature UV-vis and fluorescence spectrometries. Unique "orange-to-yellow" colorimetric transition of **3Br-1** (and **3Br-2**) dissolving in CH_2Cl_2 in the presence of 6*N* HCl (2 μl) was evidenced upon cooling the solution. The backward "yellow-to-orange" transition does occur when the stimulus was removed from the system. In contrast to CH_2Cl_2 solution, it requires heating to observe the color transition when acetonitrile was used as the solvent to study the thermochrism. The results indicated that polarity of solvents plays a decisive factor in modulating the relative stability of the neutral and protonated forms. Fluorescence intensity of **3Br-1** and **3Br-2** is quenched dramatically once protonated and can be restored by thermo stimuli. Both of compounds exhibit good thermal-stability and fatigue resistance in the processes of many heating and cooling cycles. In addition, variable-temperature ^{1}H NMR spectra reveal molecular insights of color reversibility associated with temperature changes. Our study is valuable for the construction of reversible and tunable thermochromic switches with enhanced sensitivity.

Acknowledgement, National Science Council and The Ministry of Education of Taiwan.

IMPEDANCE AND LITHIUM-7 NMR STUDIES OF SOLVENT-FREE POLYMER ELECTROLYTES BASED ON POROUS P(VDF-HFP)/P(EO-EC) MEMBRANES

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Solvent-free polymer electrolytes (SPEs) are potential materials for application as electrolytes in rechargeable lithium batteries, which are composed of materials as environmentally as possible[1]. We have developed the SPE based on porous poly(vinylidene fluoride-*co*-hexafluoropropylene) (P(VdF-HFP))/poly(ethylene oxide-*co*-ethylene carbonate) (P(EO-EC)) membranes filled with viscous P(EO-EC)[2]. These pore-filling polymer electrolytes showed relatively high ionic conductivity (ca. 3.7×10^{-5} S cm^{-1} at 298 K) and wide electrochemical stability window (0.6 ~ 5 V). In order to study a better understanding of the Li-ion mobility in polymer electrolytes, we report on impedance and ^{7}Li NMR measurements as a function of temperature in a series of polymer electrolytes.

As an electrolyte in rechargeable lithium batteries we selected the pore-filling polymer system. Porous membranes were prepared by a phase inversion method. The prepared porous membranes were filled with P(EO-EC)/$LiCF_3SO_3$ mixture and finally the solvent-free polymer electrolytes were obtained. Ionic conductivity was determined by complex impedance measurements, using a Zahner Electik IM6 impedance analyzer. The ^{7}Li solid-state NMR measurements were performed, using a modified Bruker CXP 300 NMR spectrometer operating at a ^{7}Li resonance frequency of 155.4 MHz.

The ionic conductivity of polymer electrolytes obeying Arrhenius behavior increased with increasing P(EO-EC) content in polymer electrolytes. The Li-ion mobility was investigated by measuring the linewidth of solid-state ^{7}Li NMR spectra. At the lowest temperature, the linewidths were very broad. These imply that the Li-ion is essentially immobile and thus the observed linewidths are the result of increased quadrupolar or internuclear dipole-dipole interactions. As the temperature increases, the Li-ion mobility increases enough to average out dipolar interaction, thereby producing a line narrowing. An estimation of the activation energy for polymer electrolytes can be obtained using Bloemvergeon-Purcell-Pound (BPP) theory and the following equation[3]:

$$(\Delta\nu)^2 = \left(\frac{2}{\pi}\right)\delta\varpi_o^2 \tan^{-1}(\tau_c \Delta\nu)$$

where $\Delta\nu$ is the measured linewidth, $\delta\omega_0$ is the rigid linewidth, and τ_c is the correlation time. The temperature dependence of the correlation time is assumed to follow Arrhenius behavior, which activation energies for Li-ion mobility are determined:

$$\ln\tau_c = \frac{E_a}{kT} - \ln\tau_o$$

The slope of the plot of $\ln\tau_c$ against T^{-1} yields E_a. Interestingly, the Arrhenius plots of τ_c for all polymer electrolyte samples are composed of two different regions separated by low and high temperature range and each plot shows linear type. This result is well consistent with linear behavior observed from impedance experiments in the same temperature range. It means that there is an abrupt decrease of ion mobility with decreasing temperature near 275 - 280 K (denote hereafter as T_{sc}, temperature at slope change) corresponding to the rapid change in the slope of the correlation time. Therefore, it is noteworthy to determine T_{sc} related to the abrupt deterioration of characteristic parameters (*e.g.*, activation energy and ionic conductivity). Overall results indicate that high Li-ion mobility contributes to high conductivity because it is related to the number of charge carriers and Li-ion mobility.

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VISCOELASTIC RELAXATION AS A TOOL TO INVESTIGATE THE LAYERED SILICATE STRUCTURE OF NBR-BASED NANOCOMPOSITE

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Blend of non-crosslinked acrylonitrile-butadiene copolymer (NBR) and poly(vinyl chloride) (PVC) is the representative thermoplastic elastomer (TPE). In this study, we used the layered silicate in place of the toxic sulfur for the improvement of mechanical properties and reprocessing on NBR/PVC TPE. Generally, the mechanical properties of nanocomposites depend on the degree of dispersion of layered silicate[1]. Therefore, it is expected that viscoelastic relaxation of nanocomposite may be different according to layered silicate structures.

In order to investigate the relation between viscoelastic relaxation and layered silicate sturcture, NBR nanocomposite (NC5) and NBR/PVC nanocomposite (NP73C5) were prepared by melt mixing with MMT-OH which was the montmorillonite modified with methyl tallow bis(2-hydrohexyl) ammonium and NBR or NBR/PVC blend (NP73C0), respectively. The content of MMT-OH was 5 wt% in both nanocomposites. In NP73C5 and NP73C0, the composition of NBR and PVC was a ratio of 7 to 3. For the verification of layered silicate structure, Wide angle X-ray diffraction (WXRD) was performed, and then dynamic mechanical analysis (DMA) was used to investigate of viscoelastic relaxation in both the nanocomposites.

In WXRD, a prominent peak of NC5 just is shifted toward the low angle compared to that of the MMT-OH. On the other hand, a peak of d_{001} plane of NP73C5 is completely disappeared. It implies that NC5 has the intercalated structure and NP73C5 has the exfoliated structure. Considering the processing method of NP73C5, it is interpreted that PVC changes the layered silicate structrure from intercalation to exfoliation because of polar interaction between PVC and NBR.

Empirical Havriliak-Negami (HN) function[2] is common method to determine the quantitative relaxation time, τ, by the non-linear fitting of DMA data

$$G' = G_u + \frac{(G_r - G_u)\cos\beta\theta}{[1 + 2(\omega\tau)^\alpha \cos(\alpha\pi/2) + (\omega\tau)^{2\alpha}]^{\beta/2}} \tag{1}$$

$$\theta = \arctan\left[\frac{(\omega\tau)^\alpha \sin(\alpha\pi/2)}{1 + (\omega\tau)^\alpha \cos(\alpha\pi/2)}\right] \tag{2}$$

In the relaxation time acquired HN function, it was observed that the extent of the increased relaxation time from NP73C0 to NP73C5 was higher than that from NBR to NC5 in entire temperature range. It implies that NP73C5 with exfoliated structure has more restricted molecular structure than NC5 with intercalated structure. More restricted viscoelastic relaxation in exfoliated nanocomposite is explained by the diminishment of the fast viscoelastic relaxation of polymer chains confined within nano-sized silicate layer gallery and the increase of the slow viscoelastic relaxation by the attachment of polymer chains to silicate surface[3]. Therefore, the degree of dispersion of layered silicate in polymer matrix is acquired from the extent of restricted viscoelastic relaxation. Considering that WXRD only provides information of silicate structure, the analysis of viscoelastic relaxation which can not only evaluate the viscoelastic behavior but also explain the layered silicate structure is useful to analyze of nanocomposite.

In conclusion, the investigation of viscoelastic relaxation can be used as a unique tool for characterizing the layered silicate structure.

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SYNTHESIS AND PROPERTIES OF MULTIPLY *N*-CONFUSED PORPHYRINS

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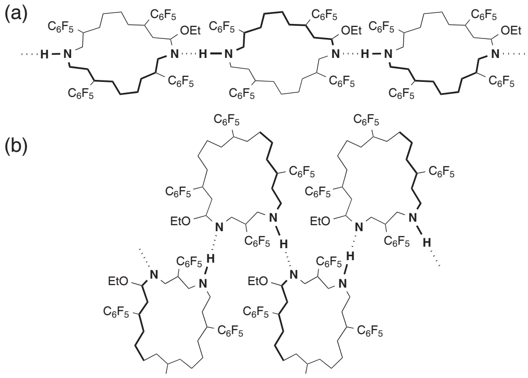
Among the increasing number of porphyrin analogs, *N*-confused porphyrin (**NCP**), in which one of the pyrrole rings is connected to *meso* carbons at α and β' positions, has been attracting considerable attention as a building block for supramolecular architectures as well as a binding receptor for cation, anion, and neutral molecules[1].



Scheme 1. 1-D hydrogen bonding networks of (a) *trans*-N_2CP and (b) *cis*-N_2CP

For example, the redox Cu^{III}/Cu^{II} potential couple for Cu^{II} complex of C_6F_5-substituted NCP can be modulated by anion-binding at the outer NH site[2]. Moreover, multiply *N*-confused porphryins such as doubly *N*-confused analogs (**N_2CP**), which are synthesized by stepwise manner, would realize multi-component oligomerization by using hydrogen bonding among two or more outer nitrogens. Actually, Cu^{III} complex of *trans*-N_2CP, wherein two *confused* pyrroles exist at the opposite sides, has exhibited hydrogen bonding 1-D rod-like nanostructure[3] as comparable with zig-zag chains of *cis*-analogs[4] in the solid state (Scheme 1). The self-assembled multiply *N*-confused porphyrins would serve as potential proton conductive wires.

HM thanks Ichikizaki Fund for the financial support.

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SYNTHESIS AND CHARACTERIZATION OF HYPERBRANCHED POLY(*ε*-CAPROLACTONE)S WITH ARCHITECTURAL VARIATION

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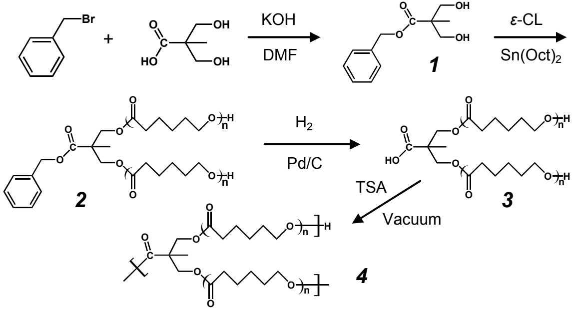
Hyperbranched poly(*ε*-caprolactone)s (HPCLs) were synthesized by moisture sensitive catalyst–free polycondensation of AB_2 macromonomers[1]. The HPCLs were designed to incorporate different lengths of linear oligomeric segments consisting of 5, 10, and 20 *ε*-caprolactone monomer units on the branched backbone chains, accordingly named as HPCL–5, –10, and –20, respectively. The synthetic pathways of HPCLs are represented in Scheme 1.



Scheme 1

Table 1. General Characteristics of Hyperbranched Poly(ε-caprolactone)s and Their Linear Counterpart

Sample	$<N_{\varepsilon\text{-CL}}>$	$<N_{AB2}>$	M_n	R_g (nm)	g
HPCL–5	5.7	8.1	11,800	4.57	0.76
HPCL–10	10.3	5.1	12,600	4.77	0.83
HPCL–20	20.1	3.3	15,700	5.18	0.98
LPCL	·	·	10,700	5.23	1

End–group analyses were performed on ^{1}H NMR spectra of HPCLs, which provided information about the average number of ε-caprolactone units incorporated in the AB_2 macromonomers, $<N_{\varepsilon\text{–CL}}>$, and the average number of AB_2 macromonomer units incorporated in the resulting hyperbranched polymers, $<N_{AB2}>$. Consequently, the number average molecular weights of HPCLs were calculated and were listed in Table 1 along with the results of $<N_{\varepsilon\text{–CL}}>$ and $<N_{AB2}>$.

Conventional size exclusion chromatography (SEC) and SEC equipped with multi-angle laser light scattering detector (SEC-MALLS) were employed to measure molecular weights and molecular weights distribution of HPCLs. Then, the results were compared with those obtained from ^{1}H NMR end–group analyses, indicating that there was a good agreement between the results from SEC-MALLS and ^{1}H NMR.

From small angle X-ray scattering (SAXS), the radii of gyration (R_g's) of the HPCLs and their linear counterpart, poly(ε-caprolactone) (LPCL) were determined from the initial slope of the reciprocal of scattered intensity, $1/I(q)$ vs the square of scattering vector, q^2, curves, fit by Zimm scattering function[2], and listed in Table 1.

The ratio of mean-square radius of gyration of each HPCL to that of LPCL, termed as branching ratio, g (eq 1)[3], resulted in the relative degree of branching for individual HPCLs and also listed in Table 1.

$$g = \frac{\langle R_g^{\,2} \rangle_{HPCL}}{\langle R_g^{\,2} \rangle_{LPCL}} \qquad (1)$$

In summary, a series of HPCLs with architectural variation was synthesized and characterized. ^{1}H NMR end–group analysis and SEC-MALLS was found to be useful to measure absolute molecular weights of HPCLs. Estimaited values of branching ratio showed that as the length of linear oligo(ε-caprolactone) segments decreased, the more highly branched polymers were obtained, i.e., HPCL–5> HPCL–10> HPCL–20.

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SYNTHESIS OF NOVEL BIODEGRADABLE POLYCARBONATES AS NON-VIRAL GENE DELIVERY VECTORS

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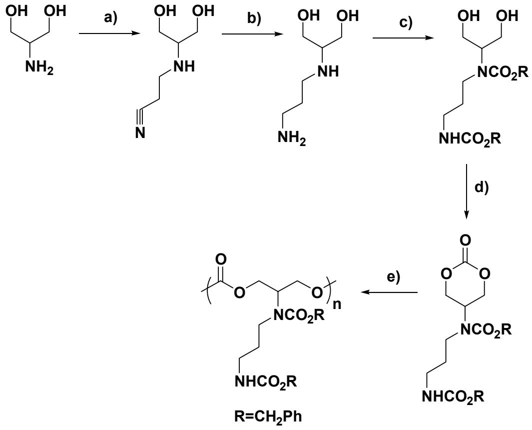
The gene carriers used so far include viral systems such as retroviruses, adenoviruses, and adeno-associated viruses or nonviral systems including liposomes and polymers. Viral vectors have been shown to have high transfection efficiency when compared to non-viral vectors, but due to several drawbacks, such as targeting only dividing cells, random DNA insertion, low capacity for carrying large therapeutic genes in size, risk of replication, and possible host immune reaction, their use *in vivo* is severely limited[1,2]. Over viral gene carriers, there are several advantages in adopting non-viral based gene therapies[3-5], including nonimmunogenicity, low acute toxicity, and flexibility to design a carrier with well-defined structural and chemical properties on a large scale. Non-viral gene delivery systems such as cationic polymers or synthetic gene carriers are being investigated intensively to circumvent some of the problems encountered with use of viral vectors.

Several polymeric materials have been investigated for use as gene carriers, and among them, biodegradable polymers are gaining attentions[6-8]. Delivering bioactive agents from the biodegradable delivery system is highly desirable because it discards the need for a surgical procedure to remove the delivery system. Controlled release of bioactive agents can reduce the frequent administration by maintaining the therapeutic concentration at a desired level, which brings the importance of the control over the degradation rate of the employed biodegradable delivery system

We have investigated the synthesis of biodegradable polycarbonates containing protonable primary amines for efficient condensing plasmid DNA and secondary amines for effective endosomal escape. Cyclic carbonate monomer was synthesized and the polymerization was carried out by anionic ring opening polymerization.The synthetic scheme for the preparation of the six-membered cyclic carbonate monomer with protected groups is shown in Scheme 1. The intermediate 3-(2-hydroxy-1-hydroxymethyl-ethylamino)-propionitrile was hydrogenated using Raney Nickel catalyst and stoichimetric amount of NH3 to amine. Primary and secondary amines in 2-(3-amino-propylamino)-propane-1,3,-diol were protected by benzyloxycarbonyl groups and the resulting diol was reacted with triphosgene in the presence of 2,3-dimethyl-phenyl-3-pyrazolin-5-one as a base to afford the cyclic carbonate monomer[9]. It was investigated by employing different ratio of the monmer to the initiator to control the molecular weight of polymer. The polymerization was not under control to produce polymers with molecular weight quite different to ther targeted one and the optimization of the polymerization condition is in progress.

In the IR spectra of the polymer, the carbonate and urethane carbonyl absorption peaks were respectively observed at 1760 and 1705 $cm^{-1,}$ to confirm that polycarbonates were successfully obtained without the formation of ether bond by elimination of CO_2 during the polymerization. GPC traces showed that the polycarbonates had bimodal distributions and the M_w/M_n values were in the range 1.10~1.15. Bimodal distribution with narrow molecular weight distributions suggested the polymerization was proceeded with two kinds of growing chains initiated by another initiator except *tert*-BuOLi. The synthesis of a new six-membered cyclic carbonate monomer having primary amine group and secondary amine group were successfully prepared.



Scheme 1. a) acrylonitrile, 55°, 30 min; b) H_2, Raney Ni, NH_3, EtOH, 30 psi, r.t.; c) benzyl chloroformate, $NaHCO_3$, H_2O/dioxane, 0 °C, 1 h; r.t.,12 h; d) triphosgene, 2,3-dimethyl-1-phenyl-3-pyrazolin-5-one, $CHCl_3$, 45 °C, 2 h; e) *t*-BuOLi, THF, -78 °C, 2 h

Polymerization was conducted via anionic ring opening polymerization to produce biodegradable polycarbonates with the molecular weights ranged from 20,000 to 44,000. Optimization of the polymerization is in progress and the effects of molecular weight, degradation rate, and density of cationic charges on cytotoxicity and transfection efficiency are under investigation.

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BIOMIMETIC BINDING PROPERTIES OF SOLID SUPRAMOLECULAR RECEPTORS

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The structure – binding affinity relationships were determined and compared for the binding of organic compounds by solid calixarenes, β-cyclodextrin, hydrophilic polymer and proteins. The capacity of the supramolecular hosts to perform the biomimetic properties was evaluated also by the comparison of their phase transition behavior and effects of temperature and hydrophobic hydration on the binding of substrate (guest) vapors by solid receptors in absence of liquid phase. Vapor sorption isotherms were obtained for these systems by static method of gas chromatographic headspace analysis.

Obtained thermodynamic results reveal a varied extent of similarity for the different properties of the studied receptors. All supramolecular hosts (*tert*-butylcalix[4]arene, *tert*-butylthiacalix[4]arene, adamantyl-calix[4]arene, 2,2'-bis(9-hydroxy-9-fluorenyl)biphenyl and β-cyclodextrin), polymer (substituted polyacrylamide), and proteins (albumin, trypsin, casein, β-lactoglobulin) are nonporous and bind organic compounds in the bulk of the receptor solid phase. The phase transition upon the guest (substrate) binding with the binding threshold by the sorbate activity were observed for all studied hosts and one protein (trypsin with a large additive of lactose)[1,2]. The most hosts and dried proteins perform a definite saturation by the guest (substrate) vapors[1-4]. No saturation of the studied polymer by the same sorbates was observed. A similar size exclusion effect was observed for the binding of monofunctional organic compounds and hydrocarbons by the dried polymer, proteins, β-cyclodextrin and two supramolecular hosts (*tert*-butylthiacalix[4]arene, and 2,2'-bis(9-hydroxy-9-fluorenyl)biphenyl). The key effect of hydrophobic hydration on the binding of organic compounds is similar for the studied polymer, β-cyclodextrin and proteins.

The support from URBR (UR.05.01.035), BRHE (REC-007) and RFBR (03-03-96188-r2003tat) is gratefully acknowledged.

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SYNTHESIS OF NOVEL PYRAZINE DERIVATIVES TOWARDS LIQUID CRISTALLINITY

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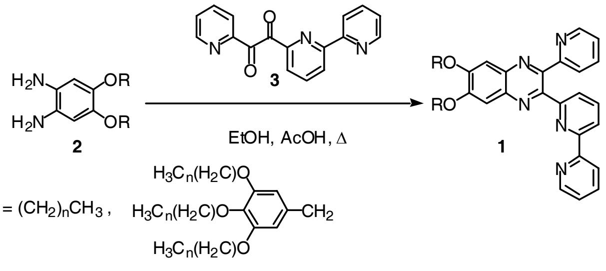
Pyrazine-pyridine hybrids form dimeric double-decker complexes with metals having tetrahedral ligand fields[1,2]. Our work concerns the use of this basic geometry to develop self-assembled thermotropic materials for applications requiring liquid crystallinity.

Quinoxaline-pyrazine ligands **1** with long-chain alkyl ethers attached to the quinoxaline benzo-ring fragment were prepared in moderate to good yields from condensation of the corresponding 1,2-diamines **2** with unsymmetrical α-diketone **3**[3]. Diamines **2** were prepared form catechol and α-diketone **3** was synthesized using our previously reported synthetic method[3].

The preparation and self-assembly behavior of bis-ligands for the formation of self-assembled highly organized, π-stacked metallorganic polymers will also be discussed.

Investigations of the stereochemistry of these complexes using special NMR spectroscopic techniques allow us to determine the solution-state stereochemistry and configuration of these complexes.



Scheme 1. Synthesis of quinoxaline-pyrazine ligands ***1***.

W*e thank the engineering and Physical Sciences Research Council (Grant R/R09138) and the EPRSC Mass Spectroscopy Centre for mass spectra.*

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SELF-ASSEMBLY OF METALLOSUPRAMOLECULAR TETRAHEDRA

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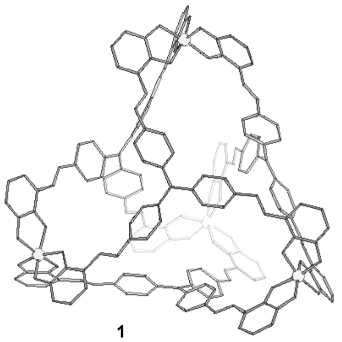
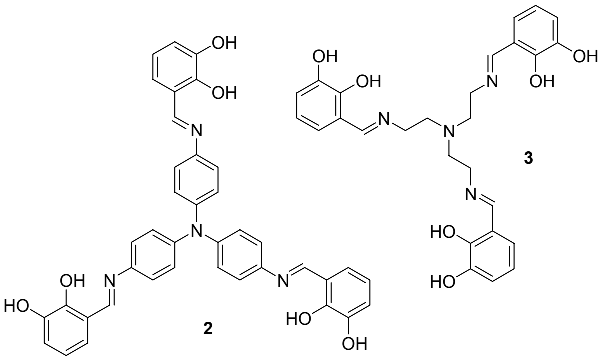
The control of the self-assembly of complicated supramolecular aggregates is an important goal to achieve which finally should enable the rational design and the preparation of functional supramolecular systems.

Just recently we started to investigate the formation of big M_4L_4 metallosupramolecular tetrahedra (like **1**) with huge internal cavities[1]. Therefore we prepared triscatecholimine derivatives **2** and **3** which possess an axis of C_3 symmetry and which smoothly lead to self-assembled tetranuclear titanium(IV) complexes. Hereby an interesting templating effect of counter cations can be observed and can be used to control the formation of well-defined supermolecules[2].



1



2 **3**

Support by the DFG (SPP 1118) is gratefully acknowledged.

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SPECTRAL INVESTIGATIONS OF FULLERENE-PORPHYRIN HYBRIDS

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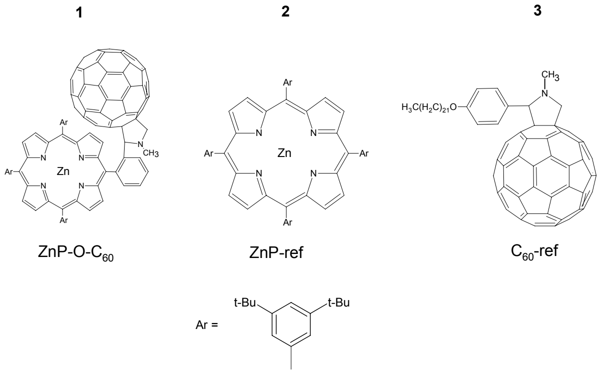
The design of functional molecular dyads that mimic photosynthetic energy transfer or can be used in electronic devices has attracted much attention in recent years. Porphyrins with their electronic absorption properties have been widely used as electron-donating scaffolds in photoactive molecular dyads. On the other hand, the unique shape of the fullerene C_{60} combined with its distinct physical properties make it a good candidate for preparation of large, supramolecular aggregates and functionalization of them. For an enhanced understanding of the chromophore interaction between fullerenes and porphyrins we performed spectral studies of some fullerene-porphyrin hybrids in a solvent-free medium.

Herein we report the UV-vis and IR absorption studies of the fullerene-porphyrin dyad, **1** consisting of porphyrin scaffold with C_{60} moiety attached to the porphyrin, **2** by short pyrrolidine single linker shown at **3** (Scheme 1). Our overall goal is to understand the correlation between the structure of new fullerene-derived systems and their spectral properties recorded in the solid state.



Scheme 1. Compounds subjected to spectral investigations in this study: fullerene-porphyrin dyad (**1**), zinc porphyrin (**2**) and modified fullerene with pyrrolidine linker (**3**).

An assignment of main electronic and vibrational bands has been made. In order to analyze experimental IR spectra of **2** a calculation of the normal vibrations for fragments of this molecule has been performed.

It was stated that significant redistribution of the charges occurs in both fullerene and porphyrin moieties upon covalent linkage. This effect is mainly observed as shifts of both electronic and vibrational bands in comparison with respective free porphyrin and fullerene features. Variable temperature IR measurements were also performed and discussed.

The authors are indebted to Professor Imahori for kind providing the samples.

SEMICONDUCTOR NANOCLUSTERS IN LANGMUIR-BLODGETT FILMS

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In the present work we report on preparation nanoclusters of semiconductor sulfide (CdS, PbS, ZnS) in Langmuir-Blodgett (LB) films and investigation of its structure and optical properties. LB films containing the semiconductor nanoclusters have potential applications in optoelectronic devices as optical switches, as infrared detectors.

The CdS, ZnS, PbS nanoclusters were fabricated by the chemical interaction of LB films of cadmium, zinc and lead behenate with hydrogen sulfide. As a result of this interaction the nanoclusters were formed in matrix of behenic acid. The structure and optical properties of nanoclusters were investigated by the high-resolution electron microscopy (HREM), UV, IR and Raman spectroscopy.

The UV-transmission spectra measured at room temperature a blue shift with respect to that of bulk crystal. The (HREM) experiments have revealed the formation nanocrystals CdS hexagonal, PbS and ZnS cubic crystalline structure with average size nanoclusters of 3±1 nm CdS and ZnS, 4±2 nm PbS.

The IR and Raman spectra reveal longitudinal optical (LO) phonons localised in nanoclusters and surface vibrational modes. The frequency of surface vibrational modes depends on the dielectric properties of surrounding media.

This work has been supported by CRDF № NO-008-X1.

PREPARATION AND CHARACTERIZATION OF A NOVEL Cu(II) TETRAAZAMACROCYCLIC COMPLEX: Cu(II) (1,8 – DI-2-PROPENYL – 1, 4, 8, 11-TETRAAZACYCLOTETRADECANE)(ClO_4)$_2$

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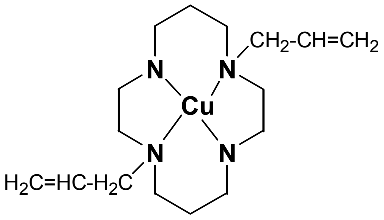
A novel Cu(II) cyclam-like complex was synthesized. The complex Cu(II) (1,8–di-2-propenyl-1,4,8,11- tetraaza-cyclo-tetradecane)(ClO_4)$_2$ was characterized by X-ray crystallograghy, UV-vis and electrochemistry. The X-ray structure indicates a *trans I* geometry with two allyl *N*-substituents on the same side of the plane.

The aqueous UV-vis spectrum shows a maximum at λ=528 nm (ε= 260 $\mathrm{M}^{-1}\mathrm{cm}^{-1}$). The cyclic voltammetry measurements show a quasi-reversible two electron wave at $E_{½}$=-0.69 V *vs*. SCE.

Detailed data will be presented.



SULFUR CONTAINING OLIGO(CYCLOHEXYLIDENES) AS ELECTRON DONORS IN CHARGE-TRANSFER COMPLEXES

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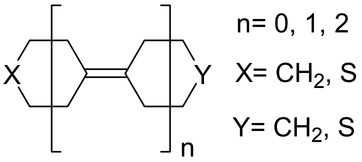
Oligo(cyclohexylidenes)[1] consist of cyclohexyl-type rings connected by olefinic bonds. They posses an alternating σ-π topology which makes them capable of charge mediation *via* a through-bond mechanism as shown by He(I) photo-electron spectroscopy and *ab initio* RHF/6-31G* calculations[2]. Hence they may find applications in molecular electronics and as active spacers in devices for supramolecular systems[3].



In this work oligo(cyclohexylidens) are studied as electron donors in charge-transfer complexes with TCNE. They are found to form weak complexes. Saturated derivatives, which lack orbital coupling, form complexes of somewhat higher energy. Separate trends for sulfur end-functionalized derivatives and non-sulfurous donors were established. The former interact preferentially with the acceptor at the sulfur site, whereas non-sulfurous compounds interact via the double bond. Complexes of TCNE and some non-sulfurous oligo(cyclohexylidenes) give an addition product.

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BINDING AND IN VITRO TRANSPORT BEHAVIOUR OF POLYOXOTUNGSTATES IN THE PRESENCE OF AMINOSACCHARIDES

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Polyoxometalates (POMs) show unique transport behaviour into living cells, and may act as antiviral and antitumoral agents[1]. Among a great variability of different metal clusters formed, Keggin type $[XW_{12}O_{40}]^{n-}$ and HPA-23 ($(NH_4)_{18}[NaSb_9W_{21}O_{86}]$: HPA-23=heteropolyacid-Na) seem to be the most important compounds for medical applications. The organic modification of the POM surface appears highly attractive to develop metallic drugs. Using such organic-inorganic hybrids, the chemical stability, the biocompatibility and the targeting may be improved. In this context, the complex formation between POMs and aminosaccharides is particularly interesting. As found recently, metal oxoanions can be efficiently bound by sorbents containing aminosaccharide-functional groups (crosslinked chitosan or 1-deoxy-1-(methylamino)-D-glucitol bound on styrene/divinyl benzene copolymer matrix)[2,3].

We want to report on the hydrolytic stability of the polyoxotungstates $Na_6W_{12}O_{39}$, $H_3[PW_{12}O_{40}]$, $K_7[Ti_2W_{10}PO_{40}]$ and $(NH_4)_{18}[NaSb_9W_{21}O_{86}]$. The binding and cellular uptake of selected polyoxotungstates in the presence of the aminosaccharides D-glucosamine, 1-deoxy-1-(methylamino)-D-glucitol and a water-soluble chitosan have been studied.

$K_7[Ti_2W_{10}PO_{40}]$ was found as the most stable compound. This polyoxotungstate has a high water solubility (>0.05 M), and was chosen for cell uptake studies. Glycolysis studies using ^{18}F-labelled FDG (fluordesoxyglucose) point to a low toxicity of $K_7[Ti_2W_{10}PO_{40}]$ in the tumor cell lines FaDu and HT-29. The cell uptake of $K_7[Ti_2W_{10}PO_{40}]$ is enhanced in the presence of aminosaccharides.

We would like to thank the International Bureau of the BMBF (project CZE 02/018) and the Grant Agency of Czech Republic (grant no. 203/01/1310) for financial support.

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SYNTHESIS AND STUDY OF THE MOLECULAR ASSEMBLIES OF THE CROWN-CONTAINING 4-STYRYLPYRIDINE

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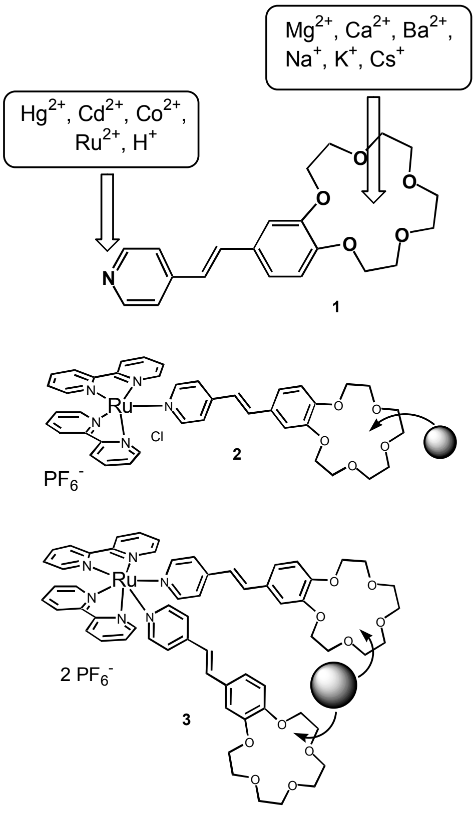

Scheme

A supramolecular assembly consists of several independent components, properly linked in a superstructure, and is capable of performing a specific function[1]. The possibility of controlling the organisation of the molecular components in the supramolecular assembly opens ways for improving substantially the characteristics of the starting components and for obtaining multicomponent systems that exhibit new properties[2].

In the present contribution the synthesis and the characterization of the 4-styrylpyridine incorporating a [15]crown–5 (**1** in the Scheme) are presented.

The compound consists of a heterocyclic residue and a benzocrown ether linked by an ethylenic double bond, and therefore it contains two binding centers: a crown ether moiety capable of forming complexes with alkaline and alkali earth metal cations and a heterocyclic residue which exhibits affinity for heavy and transition metal cations.

The complexes of Ru^{2+} containing one (**2** in the Scheme) or two (**3** in the Scheme) 4-styrylpyridine incorporating the [15]crown–5 were prepared. Their properties and binding ability toward metal cations are reported.

The study was supported by INTAS (Grant 03-51-4696), RFBR (Projects No. 04-03-32677, 03-03-32849 and 02-03-33058), Program "Integration" of the Ministry for High Education of Russia.

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CONTROL AND FORMATION OF BINARY CHEMICAL NANOPATTERNS VIA ELECTRON BEAM NANOLITHOGRAPHY AND ALKANETHIOL SELFASSEMBLY

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Using the ability of e-beam nanolithography (EBL) to create nanometer-scale regions of specified size and geometry[1], we show that binary chemical nanopatterns can be created by combining e-beam lithography with the self-assembly of alkanethiols (Fig. 1). Because the process involves the successive deposition of two alkanethiols bearing different end-groups, we first investigate the exchange between such alkanethiols[2] and ways to control it. Then, we apply this knowledge to the fabrication of binary chemical nanopatterns from thiols of identical chain length but terminated by different chemical moieties. Finally, we present first results on the control of block copolymer self-assembly by such binary templates.

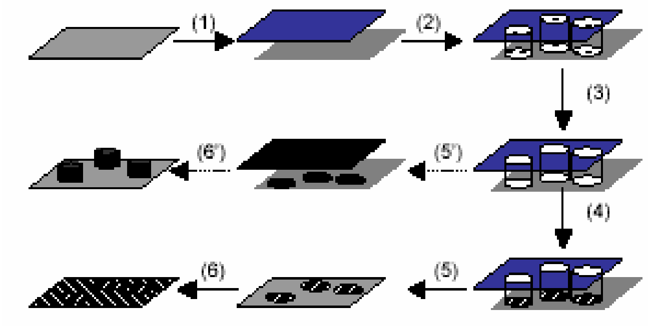

Fig. 1. Schematic representation of the nanofabrication process.

Deposition on the substrate surface of a resist layer (1); patterning of the resist layer by e-beam lithography (2); exposed zones are developed (3); thiolisation in liquid or gas phase (4); dissolution of the resist layer (5); thiolisation of the free substrate surface with another thiol (6). Lift off technique, used to verify the quality of the e-beam lithography: Ti evaporation on the substrate surface (5'); dissolution of the resist layer (6').

We are grateful to V. Bayot (UCL/DICE) for providing access to EBL facilities, to Alain Moussa for technical help, to Anne-Sophie Duwez (UCL/POLY),) for discussions about chemical aspects of monolayer formation and to Paul Rouxhet (UCL/CIFA) for providing access to the XPS and contact angle instruments. This research was supported by DG Scientific Research of the French Community of Belgium (Actions de Recherches Concertées 00/05-261 "NANORG"), by the Belgian Fund for Fundamental Collective Research (FRFC) and by the Office for Scientific, Cultural and Scientific Affairs of Belgium (Interuniversity Attraction Poles).

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STRUCTURE AND ENERGETICS OF NEW THIACALIX[4]ARENE DERIVATIVES AND ITS ZINC COMPLEX

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Thiacalixarenes have recently emerged as new members of the calixarene family and they have attracted considerable interest in the growing field of supramolecular chemistry[1]. The replacement of the usual methylene bridges by sulfur atoms modify many features in terms of complexation abilities especially with transition metal ions, conformational flexibility and reactivity. Their potential applications have been used as receptors, building blocks and molecular platforms in a wide diversity of areas such as host-guest chemistry, molecular recognition, separation chemistry and sensors.

DFT methodology using the B3LYP functional with 6-31G(d,p) basis set has been applied to study the structure, and conformational equilibrium of new thiacalix[4]arene derivatives namely tetraaminothiacalix[4]arene (**I**) and tetra mercaptothiacalix[4]arene (**II**) in which all four hydroxyl groups are substituted by amino and thiol moities, respectively[2]. The results predict the stability ordering : 1,2-alternate < 1,3-alternate < partial cone < cone, which is in a good agreement with previous theoretical study on the parent thiacalix[4]arene[3]. The intramolecular bonding between hydrogen atoms and sulfur bridges seems to be a dominant factor in stabilizing all the conformer rather than hydrogen bonds between groups of the lower rim. In this work the complexation of each one of the four conformer of the compound **I** with the Zn^{2+} ion is studied. The geometry of each complex was obtained at B3LYP/DFT level by using 6-31G(d,p) for ligand and LANL2DZ basis set for Zn. The 1,3-alternate conformer is favored to Zn^{2+} as most stable complex. The stability ordering of the complexes differs from the one predicted for the isolated conformers, and the coordination around this center ion is ensured by the nitrogen atoms and the π faces of the benzene rings, which give either tetrahedral or square planar geometry.

This work is supported by Fundação para a Ciência e a Tecnologia (LISBON) through PhD scholarship SFRH/BD/7077/2001.

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TOWARDS SMART MOLECULAR DEVICES – DISCRETE CAGES AND RECTANGLES

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Discrete molecular cages/clusters or squares/rectangles, constructed from a combination of metal ions and carefully designed organic ligands, have increasingly become highly desired target compounds[1]. This interest stems from their ability to encapsulate guest molecules. The possible applications of this encapsulation process include chiral recognition and memory[2], selective guest incorporation[3] and use as nanoscale reaction vessels[4].

Recently we demonstrated simple thioether-based ligands can be used to construct rectangular structures which form channels in the extended supramolecular network[5] (Fig. 1).

We are now starting to develop ligands for the synthesis of discrete cages/rectangles, which incorporate fluorescent moieties. Incorporation of fluorescent groups within the ligand structure will allow the synthesis of discrete hosts with optical properties that may be altered by guest interaction. Such host-guest relationships may be exploited as 'smart' switches for detection of specific guest molecules.

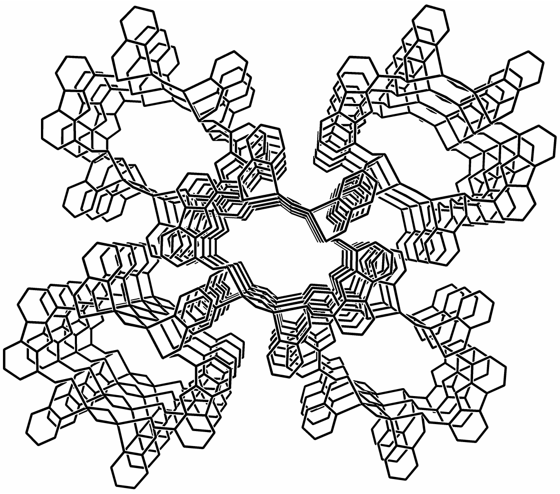

Fig. 1. $Cu_4(\mathbf{L})_2I_4$ complex [**L** = 4,6-Bis(methylsulfanylmethyl) dibenzofuran] showing the channels and interdigitation of the rectangles.

The work was funded by an Otago Research Grant and by the Foundation for Research, Science and Technology, contract: UOOX0103.

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NOVEL PHENANTRIDINIUM-NUCLEOBASE CONJUGATES AND THEIR INTERACTIONS WITH POLINUCLEOTIDES

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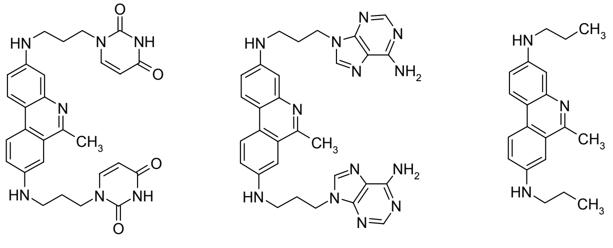
Interactions of different intercalator–nucleobase conjugates with targeted polynucleotides were an objective of intensive research in last decade. A number of conjugates were found to exhibit selective binding at complementary abasic sites in double stranded DNA / RNA[1].

The novel phenanthridinium–nucleobase conjugates were prepared (Fig. 1) and studied by spectroscopic methods. An analysis of ^1H NMR, UV-vis and fluorescence spectra in aqueous media revealed intramolecular aromatic stacking interaction between phenanthridinium unit and nucleobases, resulting with folded conformation of molecules, that was more pronounced for the adenine conjugate.



1 *2* *3*

Fig. 1. Novel phenanthridinium–nucleobase conjugates ***1-2*** and reference compound ***3***.

The results show that interactions with ss- and ds- DNA / RNA strongly depend on type of charge on phenantridinuim unit[2,3] as well as on type and number of nucleobases attached. Contrary to its analogue with one nucleobase unit[2], compound ***2*** doesn't show higher affinity to poly-U than compounds ***1*** and ***3***. Also, compound ***2*** probably binds into the major groove of ds polinucleotides, while compounds ***1*** and ***3*** bind by intercalation. Interestingly, compound ***1*** stabilises ds-poly AH^+ much stronger than ***2*** and ***3***. It can be proposed that additional A-U hidrogen bonding interactions are responsible for increased stabilisation.

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COMPLEXES OF 3-(ARYLHYDRAZONO)PENTANE-2,4-DIONES: NEW POTENTIAL BUILDING BLOCKS FOR COORDINATIVE OPEN FRAMEWORK CONSTRUCTION

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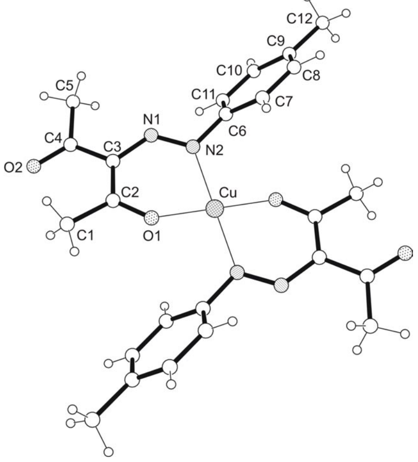
Although 3-arylhydrazones of 2,4-dicarbonyl compounds are known for more than 100 years[1], this class of compounds has remained rather unacknowledged in the literature, and so far only very few X-ray crystal structures of respective compounds have been described[2].

On the other hand, compounds of this type were found to readily form complexes with transition metal ions, and it has also been shown that the free arylhydrazone ligands are formed via a simple Japp-Klingemann reaction between an aromatic diazonium salt and the 1,3-dicarbonyl compound in a methanolic solution containing sodium acetate[3]. Hence, a new potential building block for coordinative open framework construction might arise from such a promising property.



Scheme 1. Typical coordination mode of a Cu(II) complex.

This prompted to study 3-(arylhydrazono)pentane-2,4-diones and metal ion complexes of this compound class more deeply. From this point of view, preparation of respective compounds including Cu(II) and Ni(II) complexes are described, and X-ray crystal structures of free hydrazone ligands and complexes are discussed, showing potential use in the synthesis of new metal-organic materials.

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A NEW PYRIDINE-BASED 12-MEMBERED MACROCYCLE FUNCTIONALISED WITH DIFFERENT FLUORESCENT SUBUNITS: OPTICAL RESPONSE TO Cu^{II}, Zn^{II}, Cd^{II}, Hg^{II} AND Pb^{II}

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Fluorescent sensors for charged and neutral species have attracted great attention in the past decade due to the low detection limits that can be achieved and relatively cheap equipment used. In these molecular sensors the selective hostguest interaction between the target species and the receptor unit can cause a fluorescence enhancement or a quenching of the fluorogenic fragment[1-4].

In this contest, a new pyridine-based 12-membered macrocycle has been synthetised and functionalised with three different fluorophores (9-methylanthracene, 8-hydroxyquinoline and dansylamide) (Fig. 1).

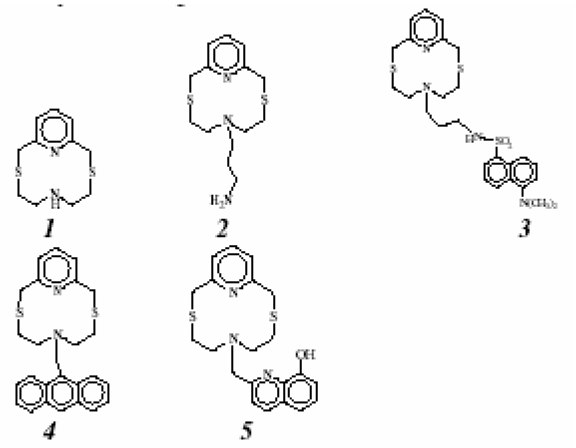

Fig. 1. The five new ligands synthetised

The coordination properties of the free macrocycle ***1*** and of its propylamine pendant arm derivative ***2*** towards Cu^{II}, Zn^{II}, Cd^{II}, Hg^{II} and Pb^{II} have been investigated both in solid state and in aqueous solution.

UV-vis and fluorimetric titrations of ***3***, ***4*** and ***5*** with the above mentioned metal ions have been performed in $MeCN/H_2O$ (4:1 v/v). The fluorescence of ***3*** is quenched after addiction of one equivalent of Cu^{II} and Hg^{II}, while the luminescence intensity of the quinoxaline group is switched on upon addiction of Zn^{II} and Cd^{II} in the case of ***5***. The emission properties of ***4*** are instead altered with all metal ions investigated.

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SYNTHESIS OF A NEW MACROCYCLIC POLYTHIAETHER-DIESTER LIGANDS

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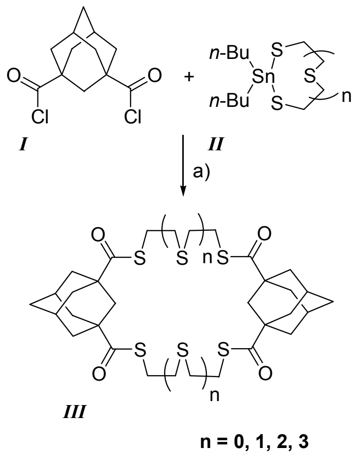
In recent years considerable effort has been made to design syntetic complexing agents, for metal ions and charged molecules. Thiacrown ethers have been studied chiefly for their capacity to ligate transition metal ions. They bind second- and third- row transiton metal ions and generally stabilize the lower oxidation states of these ions[1].



Scheme 1. a) $CHCl_3$

Various modifications have been made to the basic crown thiaether structures in attempt to enhance the selectivity of these ligands and the stabilities of complex formed. Among these modifications are the inclusion of ester linkages[2] and polycyclic moietys[3] in the polyether ring.

We describe here the synthesis of several new macrocyclic polythiaether-diester compounds, containing the 1,3-bridged adamantyl moiety which function as a rigidifying ‘’spacer’’ and also serves to confer a degree of preorganization upon the macrocyclic thiaether (Scheme 1).

We also highlight the use of novel family of stannanthianes as activated dithiols for the efficient preparation of macrocyclic thialactones.

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STUDY OF DISSOCIATION KINETICS OF EUROPIUM(III) COMPLEXES OF DOTA DERIVATIVES BY TIME-RESOLVED FLUORESCENCE LASER SPECTROSCOPY (TRFLS)

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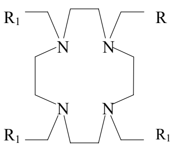
Ln(III) complexes of *DOTA* (1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetate) and their analogues are used for their high thermodynamic stability, kinetic inertness and other properties as MRI probes[1] or fluorescent labels for immunoassays (Eu(III), Tb(III))[2] in medicine. New analogues of *DOTA* were prepared by substitution of one acetic group by pendant groups containing phosphonic group. Eu(III) complexes of *DO3A* and *DOTA* analogues containing phosphonic pendant group were investigated.



R_1	R_2	
COOH	H	***DO3A***
COOH	COOH	***DOTA***
COOH	$P(O)(OH)_2$	***DO3AP***
COOH	$P(O)(OH)(CH_2)_2COOH$	***DO3AP^{PrA}***
$P(O)(OH)_2$	$P(O)(OH)_2$	***DOTP***

TRFLS of the europium(III) ion (lifetime measurements of the excited state and excitation spectroscopy of the $^7F_0 \leftarrow {}^5D_0$ transition) is a useful tool to study the first coordination sphere of the metal ion in those complexes. The number of coordinated water molecules in europium(III) complexes ranges from 0 (*DOTP*), 1 (*DO3AP*, *DO3AP^{PrA}*), 3 (*DO3A*) to 9 (Eu(III) perchlorate). Luminescence lifetime studies were employed for the determination of the number of water molecules coordinated to the Eu(III) ion of the complex during the complex dissociation in order to propose the reaction mechanism.

It has been observed under extreme experimental conditions (in 3 mol.l^{-1} $HClO_4$ at 21°C) that the rate of dissociation of the europium(III) complex increase in the order DO3A < DO3AP < DO3AP^{PrA} < DOTP.

This work was supported by grants (GA CR 203/02/0493 and 203/03/0168), Ministry of Education, Youth and Sports (26/2004/CZ) and performed in frame of the EU COST D18.

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DOUBLE AROMATICITY IN MONOCYCLIC BORON CLUSTERS

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The stability of conjugated molecules obeys the Huckel rule, which states that monocyclic conjugated molecules with 4n+2 π-electrons are stable, while monocyclic conjugated molecules with 4n π-electrons are unstable. The rule arises from the out-of plane π molecular orbitals. There is another kind of π molecular orbitals called in-plane π molecular orbitals. The aromaticity for this π molecular orbitals is called in-plane aromaticity. Monocyclic boron clusters have these two kinds of π molecular orbitals. So it is expected that monocyclic boron clusters have the double aromaticity, out-of-plane aromaticity and in-plane aromaticity.

In the present paper we used the geometry criterion and electron count criterion to explore the double aromaticity/antiaromaticity concept of monocyclic boron clusters.

We optimized the monocyclic boron clusters in singlet state with D_{nh} symmetry as initial structures. We obtained the optimized structures with D_{nh} symmetry for B_4 , B_8 and B_{12} , but could not obtain such structures for B_6 and B_{10}. The analysis of frequencies reveals that only B_{12} cluster with D_{12h} symmetry is a minimum on the potential energy surface and B_4 and B_8 with D_{nh} symmetry are not minima. Triplet B_6 and B_{10} clusters with D_{nh} symmetry were found to be stationary points on the potential energy surface.

The results of the calculations show that the numbers of out-of-plane π -electrons in B_4, B_8 and B_{12} are 2, 6 and 6, respectively, and the numbers of in-plane π-electrons in B_4, B_8 and B_{12} are 2, 2 and 6, respectively. Therefore B_4, B8 and B_{12} are doubly aromatic from the electron count. However, since B_4 and B_8 in D_{nh} structure are unstable, these two clusters are not aromatic. Only B_{12} in D_{12h} structure is doubly aromatic from both the geometry criterion and electron count criterion.

The numbers of out-of-plane and of in-plane π-electrons in B_6 and B_{10} have the different modes. Namely, the numbers of out-of-plane and of in-plane π-electrons in B_6 are 4 and 2, respectively, and the numbers of out-of-plane and of in-plane π-electrons in B_{10} are 6 and 4, respectively. So monocyclic B_6 cluster has the out-of-plane anti-aromaticity and in-plane aromaticity and monocyclic B_{10} cluster has the out-of-plane aromaticity and in-plane anti-aromaticity. In general the effect due to anti-aromaticity is larger than that due to aromaticity. Therefore these clusters are expected to be unstable. This agrees with the result of calculations which shows that these two clusters have no stationary points at D_{nh} structure.

INCLUSION COMPLEXES BETWEEN 3,3'-SUBSTITUTED[*n*]STAFFANES AND β-CYCLODEXTRIN IN WATER

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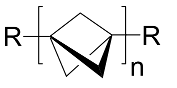
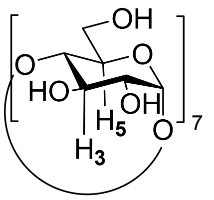
Axially substituted [*n*]staffanes *I* form inclusion complexes with β-cyclodextrin (*II*) in water. ^1H NMR spectrum of a water solution of β-cyclodextrin *II* has shown apparent changes of chemical shifts of intracavity protons H-3 and H-5 upon addition of [*2*]staffane-3,3'-diol (*Ia*) into the solution. Nuclear Overhauser effect has been observed between β-cyclodextrin protons H-3, H-5 and bridge protons of the diol *Ia*. The method of continuous variations applied to the both complexation sensitive chemical shifts revealed formation of host-guest complex of 1:1 stoichiometry[1].



I

Ia: R=OH; n=2
Ib: R=I; n=1
Ic: R=I; n=2
Id: R=TMS; n=2



II

$$Ia + II \xrightleftharpoons{K_{11} = 3015\ M^{-1}} Ia \cdot II$$

The association constant $K_{11} = 3015\ M^{-1}$ of complex formation in water has been obtained from NMR shift titration[2] of 2 mM β-cyclodextrin solution with [*2*]staffane-3,3'-diol at 303K. [*n*]Staffanes *Ib-d* bearing lipophilic groups at bridgehead positions form sparingly soluble complexes with β-cyclodextrin upon mixing in D_2O/DMSO-d_6 solvent mixture precluding their study by solution NMR methods. The results represent first example of host-guest complex formation utilizing bicyclo[1.1.1]pentane derivatives, formerly recognized potential building blocks for supramolecular chemistry[3,4].

Financial support from Ministry of Education, Youth and Sports of the Czech Republic (projects ME 571 and FRVŠ 574/G6/2003) is acknowledged with thanks.

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USING WELL-DEFINED EO_mMA_n DIBLOCK COPOLYMERS AS TEMPLATES FOR SYNTHESIS OF MESOPOROUS SILICAS WITH DIFFERENT STRUCTURES

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For AB diblock copolymer, it is believed that degree of polymerization ($N = N_A + N_B$), the composition ($f_A = N_A/N$), and Flory-Huggins interaction parameter χ_{AB} are major factors to affect the mesostructure of their micro-phase. In a recent work, we found that with a careful tuning the composition (f) and combination parameter (χN) of copolymer, the *Ia3d* cubic mesoporous silica could be synthesized by using a proper process and composition of poly(ethylene oxide)-*b*-poly(methyl acrylate) [denoted as EO_nMA_m] diblock copolymer ($EO_{23}MA_{17}$). Herein, we reported the details of the preparation of the well defined diblock copolymers EO_mMA_n and the use of these copolymers for the construction of mesoporous silica with various pore size in a wide dimension of 4.0-20.0 nm.

To prepare precisely the desired amphiphilic block copolymers is one of the primary works of this study. The methyl-capped polyethylene oxide, a commercial available reagent with well-defined units, was used for the hydrophilic portion of the polymer. Treatment of the alcohols with α-bromo-isobutanoyl bromide yielded the desired macro-initiator, which was suitable for building the block of poly(methyl acrylate). Without any solvent, methyl acrylate was polymerized in the presence of macro-initiator and copper(I) chloride and the ligand to form the diblock copolymers (EO_nMA_m)

The mesoporous silicas were synthesized from the EO_nMA_m-TEOS-HCl-H_2O compositions. Obviously, this mesoporous silica after -calcination at 560 °C exhibits three sharp XRD peak at low-angle, which are the characteristic of the large hexagonal unit cell. By the observations of the TEM, the sample exhibits both the well-ordered hexagonal-array-pore and parallel-channel images, resembling to those from a -SBA-15 mesoporous silicas. The N_2 adsorption-desorption of the $EO_{17}MA_{12}$-templated mesoporous silica shows a sharp capillary condensation at P/P_0 of about 0.5 and adsorption volume ~ 420 cm^3/g, STP. This indicates that the mesoporous silica has uniform pore size and large porosity and surface area (BET surface area ~ 600 m^2/g).Various chain length of the diblock copolymers EO_nMA_m were used as templates to construct the mesoporous silica. This study allows us to know better on the self-assembly of diblock copolymers.

This research was supported by Ministry of Education, Taiwan through the Area of Excellence program.

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SYNTHESIS AND SPECTRAL CHARACTERIZATION OF A NOVEL QUATERNARY ALKYL AMMONIUM PORPHYRIN-CHOLIC ACID AMIDE

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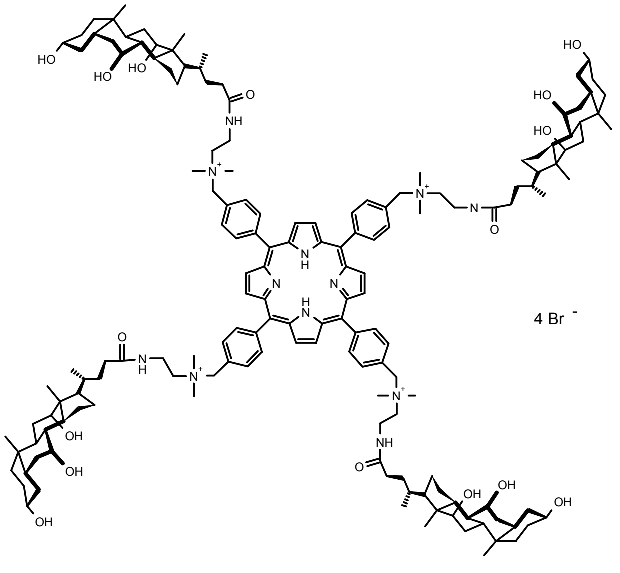

Scheme. Structure of **1**.

We report a synthesis and spectral characterization of a novel quaternary alkyl ammonium porphyrin-cholic acid amide **1** (Scheme), which was prepared by the previously reported procedure[1,2]. The starting porphyrin derivative was prepared according to the procedure of ref.[3]. **1** was characterized by 1 D ^1H, ^{13}C as well as 2 D homo- and hetero-nuclear NMR, and ESI-TOF MS measurements.

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GUANINE QUARTETS: CATION-INDUCED SELF-ASSEMBLY STUDIED BY VIBRATIONAL CIRCULAR DICHROISM SPECTROSCOPY

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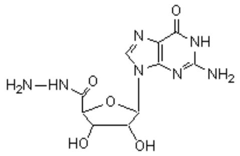
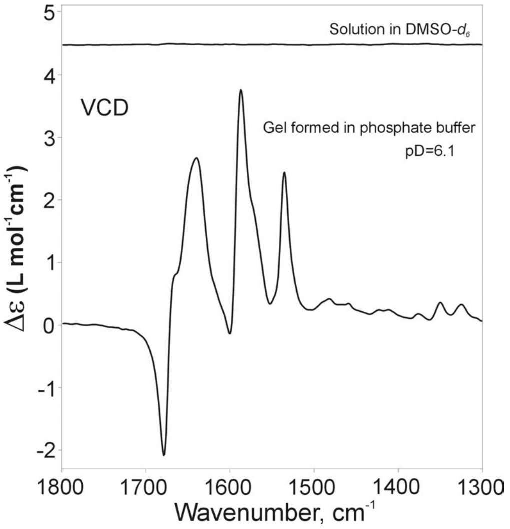


G-1



Guanine derivatives are important motifs in nanotechnology and supramolecular chemistry[1,2]. Our newly synthesized chiral derivative ***G-1*** can form the gel in presence of alkali metals (Na^+, K^+) in D_2O and H_2O, while the liquid solution is produced in DMSO-d_6. The gelation process is accompanied by the chirality variation, which was studied using vibrational circular dichroism (VCD) spectroscopy. Temperature stability and influence of the particular solvents on structure of ***G-1*** are discussed based on the VCD and infrared absorption spectra.

The work was supported by the research grants of Ministry of Education, Youth, and Sports of the Czech Republic (1K03012 and MSM 223400008).

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CRYSTAL STRUCTURE OF TETRAPHENYL-PHOSPHONIUM CHLORIDE DI-PERHYDRATE

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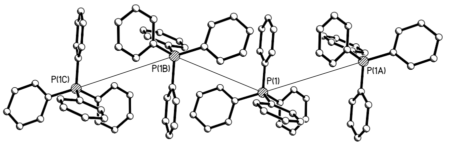
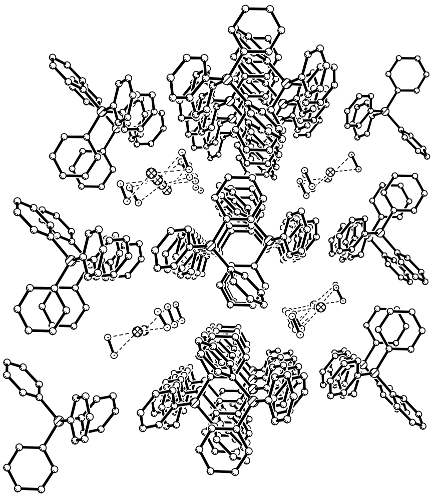
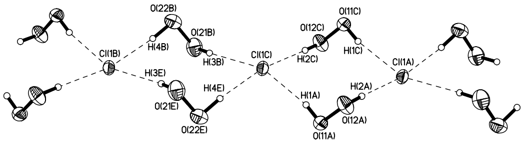
The crystal structure of the title compound was determined by X-ray diffraction studies. Bulky tetraphehylphosphonium cations are linked by six-fold phenyl embraces (6PE) forming infinite zigzag chains ZZI6PE along the *b*-axis. The P-P distances are of ordinary values for 6PE interactions between adjacent Ph_4P^+ cations (6.347, 6.709 Å).



These chains are separated by wide channels filled with Cl^- anions and H_2O_2 molecules (projection along the *b*-axis).



Hydrogen peroxide and Cl^- anions are combined into infinite chains by approximately linear O-H…Cl hydrogen bonds. H…Cl distances are within the range 2.05(4) – 2.24(4) Å.



To the best of our knowledge, this is the first example of the structure where solvent H_2O_2 molecules serve as donors of hydrogen bonds only. Both independent H_2O_2 molecules represent screw geometry with H-O-O-H torsion angles equal to 89(2) and 95(3)°.

A.V.C. and L.G.K. are grateful to The Royal Society and INTAS (grant 03-51-4696).

BIOORGANIC RECEPTORS FOR SMALL PEPTIDES: COMBINING RATIONAL DESIGN WITH COMBINATORIAL CHEMISTRY

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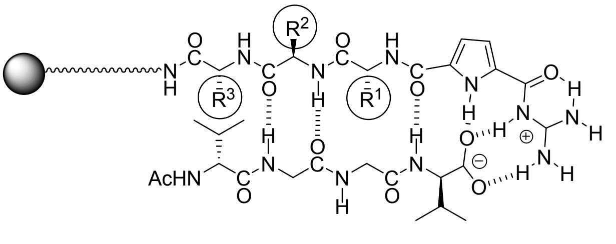
We recently found that 2-(guanidiniocarbonyl)-1*H*-pyrroles efficiently bind carboxylates by ion pairing in combination with multiple hydrogen bonds even in water. These guanidiniocarbonyl pyrrole cations can be used as receptors for the side chain selective and stereoselective complexation of amino acids carboxylates in aqueous solvents[1-4]. Furthermore, by incorporating this recognition motif into a combinatorial receptor library, we could identify receptors for the effective complexation of biologically relevant oligopetide models. In this context, a new class of one-armed tripeptide based cationic guanidiniocarbonyl pyrrole receptors is shown to strongly bind the tetrapeptide Val-Val-Ile-Ala, representing the *C*-terminus of the amyloid β-peptide even in water[5,6]. A medium sized combinatorial library of 512 receptors was synthesized on a solid support and their binding properties determined both on bead and in solution using a quantitative fluorescence assay and UV titrations. The binding constants are in the order of 10^3-10^4 M^{-1} for the most efficient ones but differ by more than a factor of 200 among the library members.



Based on the binding data of 20 receptors a structure-stability-relationship was established for peptide binding by this new receptor class. Complex formation is controlled by a fine balanced interplay of hydrophobic and electrostatic interactions with non of these two interactions alone being strong enough to ensure complexation under this polar conditions.

Financial support by the DFG and the Fonds der Chemischen Industrie is gratefully acknowledged.

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HIGHLY STABLE SELF-ASSOCIATION OF GUANIDINIOCARBONYL PYRROLE CARBOXYLATE ZWITTERIONS IN AQUEOUS SOLVENTS: FROM DIMERS TO SUPRAMOLECULAR OLIGOMERS

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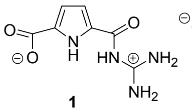
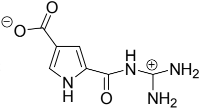
Based on a novel recognition motif for carboxylates, the guanidiniocarbonyl pyrroles, new supramolecular structures were designed. Self-complementary guanidiniocarbonyl pyrrole/carboxylate zwitterions form intramolecular loops, dimers or oligomers depending on the molecular structure of the zwitterion and the experimental conditions. Zwitterion ***1*** forms extremly stable 1:1 dimers which are held together by an extensive hydrogen bonding network in combination with two mutual interacting ion pairs as could be shown by ESI MS and x-ray structure determination[1]. Even in water, ***1*** dimerizes with an association constants of 170 M^{-1}. Hence, zwitterion ***1*** belongs to the most efficient self-assembling systems based solely on electrostatic interactions reported so far.



1



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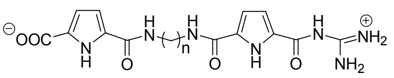

n = 2,4

3

The regioisomeric zwitterion ***2*** cannot dimerize, but forms linear oligomers in DMSO[2]. Concentration dependent NMR studies at different temperatures allowed to calculate the corresponding binding constants and thermodynamic parameters which show that the oligomerization is endothermic and therefore an entropy driven process. With more flexible zwitterions such as ***3***, the self-association properties depend on the length of the spacer[3]. In addition to linear oligomerizations (n = 2), an intramolecular self-association can occur (n = 4).

Financial support by the DFG and the Fonds der Chemischen Industrie is gratefully acknowledged.

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DIASTEREOSELECTIVE SELF-ASSEMBLY OF DINUCLEAR HELICATES USING BINOL AS CORE

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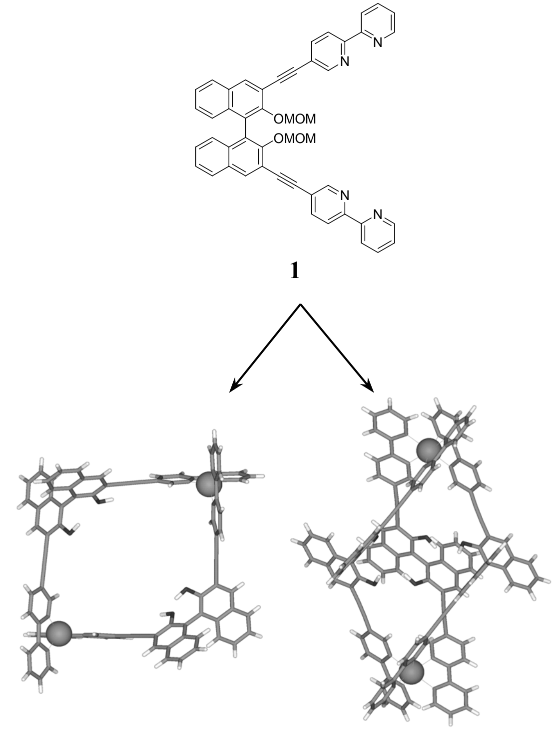
We were able to synthesise a bis(bipyridyl) substituted BINOL ligand which is able to form discrete dinuclear helicates in diastereoselective self-assembly processes[1].



1

$[\mathrm{Cu}_2\{(S_a)\text{-}\mathbf{1}\}_2]^{2+}$ $[\mathrm{Zn}_2\{(S_a)\text{-}\mathbf{1}\}_3]^{4+}$

Scheme 1. Ligand **1** and its silver and zinc complexes .

Due to the poor solubility of these complexes we decided to modify the bypiridine building block by introducing alkyl or aromatic side chains. Furthermore, we also would like to modify the spacer in order to vary the size of the cavity.

Here we would like to present the synthesis of these new ligands and their metal complexation abilities.

We thank Prof. Dr. P. Köll for providing us with excellent working conditions. Financial support from the DFG (SPP 1118 is gratefully acknowledged.

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DIASTEREOSELECTIVE SELF-ASSEMBLY OF DINUCLEAR HELICATES USING THE V-SHAPED CORE OF TROEGER'S BASE

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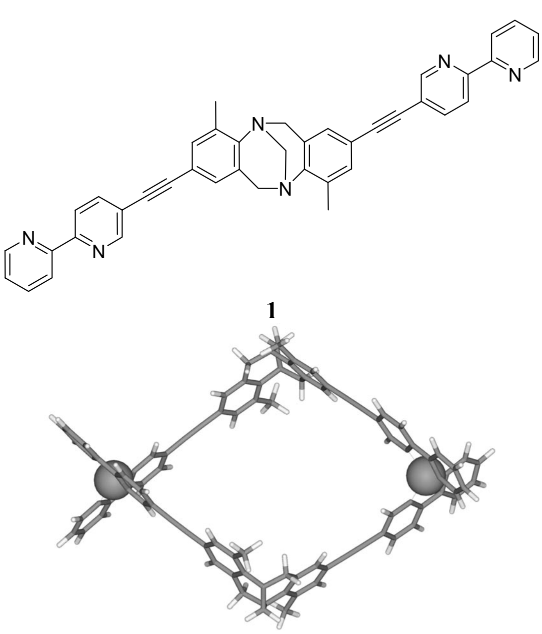
Troeger's base was first synthesised[1] more than hundred years ago in 1887. Its V-shaped structure and rigid conformation make it an almost ideal building block in order to introduce curvatures into concave receptor molecules[2].



1

Fig. 1. Ligand **1** and its dinuclear copper(I) complex **2**

The integration of the Troeger's base core into such receptors attracted our interest and several new versatile difunctionalized analogues with extended V-shaped cores could be synthesised[3]. Within the course of our studies concerning the formation of self-assembled supramolecular receptors, the 2,2'-bipyridine moiety linked to a recognition unit by certain spacers has proven to be a powerful coordination site for several self-assembled metal complexes of helical shape[4]. Application of this concept to the Troeger's base core led to such a ligand as shown below, whose diastereoselective self-assembly with silver(I)ions could be determined by NMR and MS techniques.

We thank Prof. Dr. P. Köll for providing us with excellent working conditions. Financial support from the DFG (SPP 1118 is gratefully acknowledged.

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RECOGNITION BEHAVIOUR OF 2,2'-BIS(MOM-BINOL) SUBSTITUTED 9,9'-SPIROBIFLUORENES TOWARDS AMINO ACID ESTER HYDROCHLORIDES

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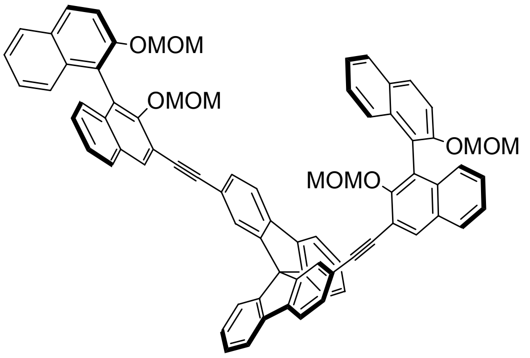
We were able to synthesise a series of enantiomerically pure bis(MOM-BINOL) substituted 9,9'-spirobifluorenes. Studying these compounds by mass spectrometric means we found that these cleft-type structures do readily form complexes with ammonium ions under conditions of ESI-MS.



Scheme 1. Cleft-type receptor structure.

Due to this fact we decided to investigate this recognition behaviour in more detail using chiral ammonium ions like protonated amino acid esters. Preliminary investigations showed that these are also good substrates to form host-guest complexes under the conditions of ESI-MS. Moreover, we were able to observe chiral discrimination by changing the configuration of the amino acid ester in two consecutive ESI-MS-experiments with the same enantiomerically pure cleft. To minimise the influence of the experiments conditions we decided to use the enantiomer-labeled guest method to gain further and more exact insight in this phenomena[1].

Here we would like to present the synthesis of the tetra(MOM) protected receptor and the results of the evaluation of its recognition behaviour towards amino acid ester hydrochlorides by using the enantiomer-labeled guest ESI-MS method. Furthermore, we will also present first results from the NMR studies of this phenomenon in solution phase.

We thank Prof. Dr. P. Köll for providing us with excellent working conditions. Financial support from the Fonds der Chemischen Industrie is gratefuly acknowledged.

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SYNTHESIS AND RECOGNITION BEHAVIOR OF ALLOSTERIC HEMICARCERANDS

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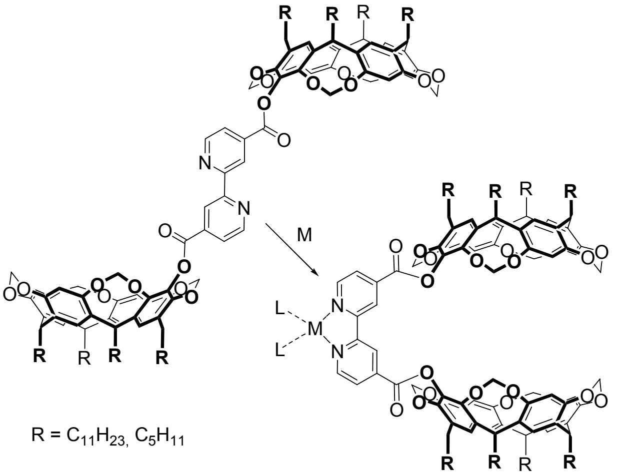

With the emergence of supramolecular chemistry resorcinarenes became interesting compounds due to their unique properties in molecular recognition. Especially container molecules - also called carcerands and hemicarcerands - have been studied extensively in this context[1].

We were able to synthesize an allosteric analogon consisting of two resorcinarene moieties linked by a 2,2'-bipyridine unit. Complexation of suitable metal ions switches the conformation towards a hemicarcerand like structure which allows to bind guest species[2].

Synthesis, complexation and recognition behavior of these receptors and further investigations leading to two new receptor systems will be presented.

We thank Prof. Dr. P. Köll for providing us with excellent working conditions. Financial support from the Fonds der Chemischen Industrie and the DFG is gratefully acknowledged. O.H. would like to thank the state of Lower Saxony for a doctoral grant.

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REMARKABLE DIFFERENCES IN THE RECOGNITION PORPERTIES OF COVALENTLY AND NON-COVALENTLY ASSEMBLED RECEPTOR STRUCTURES

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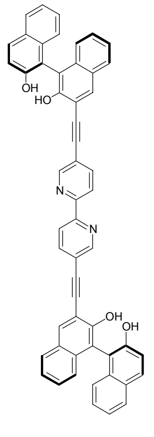
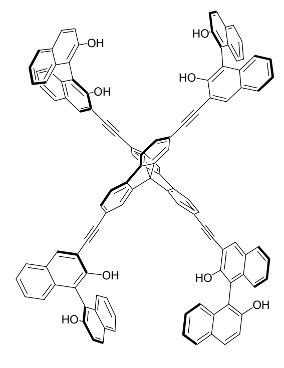


(*all-S*$_a$)-**1**



(*all-S*$_a$)-**2**

The development of receptors for the recognition of carbohydrates is an ongoing challenge in supramolecular chemistry[1]. We were able to prepare a bis(BINOL) substituted 2,2'-bipyridine (**1**) that forms dimeric mononuclear metal complexes with copper(I) or silver(I) ions[2]. Also, we were able to synthesise a covalently assembled tetrafunctionalised 9,9`-spirobifluorene (**2**), a structural analogue of these coordination compounds[3].

Here we would like to present our findings about the remarkable differences in the recognition behaviour of these two receptors towards monosaccharides.

We thank Prof. Dr. P. Köll for providing us with excellent working conditions. Financial support from the Fonds der Chemischen Industrie and the DFG is gratefully acknowledged.

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DINUCLEAR TITANIUMCOMPLEXES AS MODELS OF ACTIVE SITES OF PROTEINS

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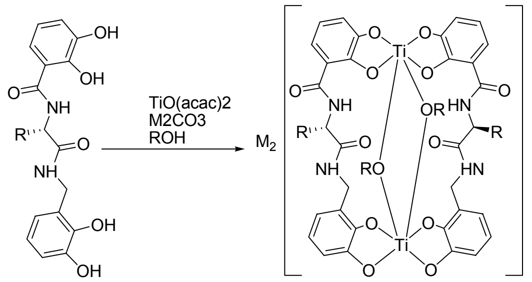
The self-assembly of amino acid-bridged dicatechols with titanium (IV) ions allows access to dinuclear complexes[1], which show structural features similar to the active sites of dinuclear metalloenzymes. Due to the amino acids, the formation of a chiral pocket is observed, in which alkoxide coligands are fixed by coordination to the two metal centers. The aim of our recent research is to enable additional weak interactions between the amino acid-side chain an functionalized alkoxide coligands.

The present strategy to prepare the ligands allows to introduce almost any amino acid as spacer and therefore gives access to a high diversity of complexes[2].



Scheme 1. Synthesis of complexes.

Currently we are investigating the introduction of more functionalized alkoxides and artifical amino acids[3] and the possibility to perform chemical reactions in the ligand sphere of the complexes.

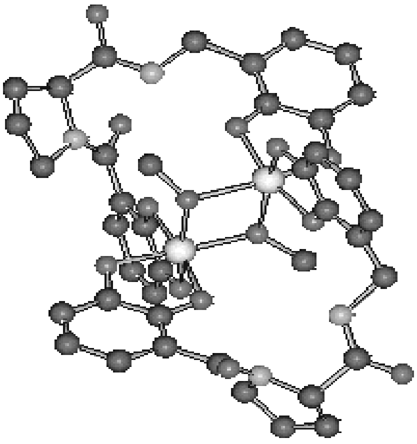


Fig. 2. X-ray structure of complex with proline as ligand spacer.

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STEREOSELECTIVE SYNTHESIS OF TRIPLE-STRANDED DINUCLEAR HELICATES

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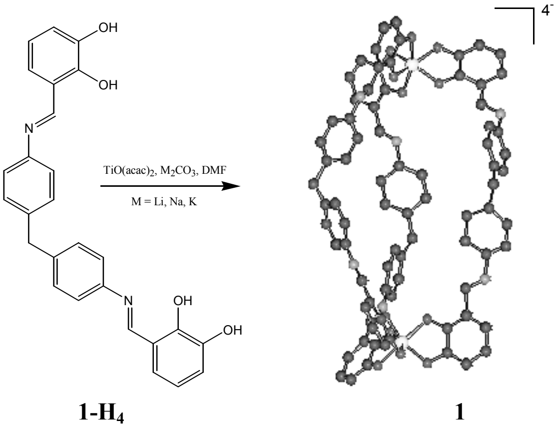
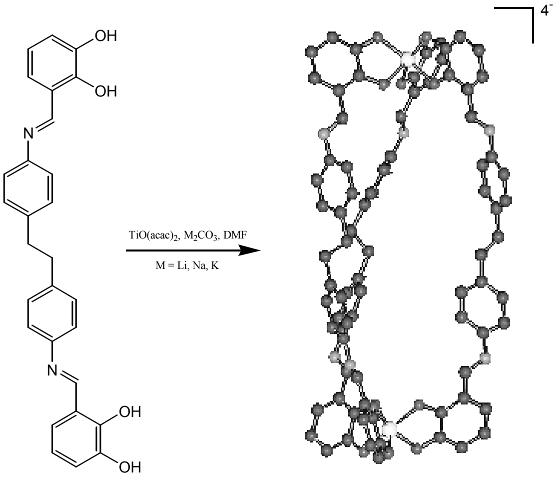


1-H$_4$ **1**

Scheme 1. Synthesis and X-ray structure of the meso-helicate **1**.

Using a chiral 1,2-diamino-cyclohexyl spacer leads to a enantiomeric pure triple-stranded dinuclear helicate.



2-H$_4$ **2**

Scheme 1. Synthesis and X-ray structure of the the helicate **2**.

The self-assembly of the two bisimine-bridged dicatechol ligands **1-H$_4$** and **2-H$_4$** with titanium(IV)-ions leads to triple-stranded dinuclear helicate-type complexes with a length of up to more than two nm. X-ray structural analysis as well as NMR investigations at variable temperatures show, that in case of the rigid linear ligand **1-H$_4$** the homochiral helicate is formed diastereoselectively. Ligand **2-H$_4$** leads with high selectivity to the formation of the heterochiral meso-helicate[1].

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ARRANGEMENT CONTROL OF AROMATIC HYDROCARBONS IN LIQUID CRYSTAL STATE

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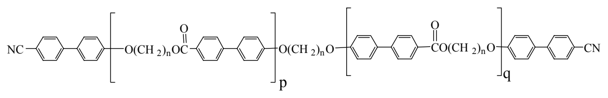
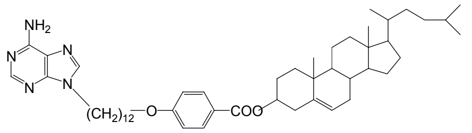
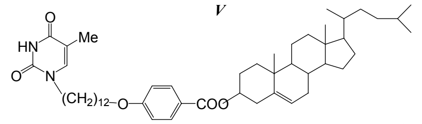
An introduction of a non-liquid crystalline molecule such as an aromatic hydrocarbon into liquid crystal affects on the dynamic order pattern. We have studied the arrangement control of the aromatic hydrocarbon in a liquid crystal state of the mixture of the liquid crystalline molecule and the aromatic hydrocarbon. A new series of liquid crystal oligomers ***I, II, III***, and ***IV*** were synthesized for the present research. In the present investigation, interesting results concerning the differences of anthracene and p-terphenyl was found out in the treatment with the liquid crystal oligomer or the molecular assembly between the adenine derivative ***V*** and the thymine derivative ***VI***. The remarkable results are summarized as follows.



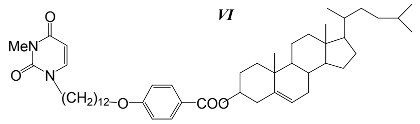
I Trimer p=1; q=0   n=3-12
II Tetramer p=1; q=1
III Pentamer p=2; q=1
IV Hexamer p=2; q=2



V



VI



VII

1) The phase-separation between the liquid crystal oligomer and the aromatic hydrocarbon depended on the ratio of the aromatic hydrocarbon to the oligomer. The ratio increased with increasing the number of the mesogenic groups in the oligomer.

2) Adding a large amount of anthracene into the tetramer ***II*** (*n*=12) resulted in a change from smectic A phase to nematic phase.

3) The mixture of the trimer ***I*** (*n*=10) and anthracene exhibited only the nematic liquid crystallinity without being related to the addition of anthracene. On the other hand, when the trimer ***I*** (*n*=10) was mixed with *p*-terphenyl in the ratio of 1 to 1, the mixture exhibited three liquid crystalline phases, *i.e.*, nematic, smectic A, and smectic E phases. The arrangement of the aromatic hydrocarbons in the liquid crystal oligomers will be discussed.

4) A glassy solid was obtained upon cooling the cholesteric liquid crystal state of the equimolar mixture of ***V, VI*** and *p*-terphenyl. On the other hand, a similar treatment of the equimolar mixture of ***V, VI***, and anthracene resulted in a characteristic crystal growth of anthracene in a spiral arrangement, after cooling slowly down to room temperature from the cholesteric liquid crystal state. A similar crystal growth in a spiral arrangement was not however obtained from the mixture containing 3-methyluracil derivative ***VII*** instead of ***VI***, suggesting that the base pairing played an important role in the crystal growth. The mechanism of the crystal growth in the spiral arrangement will be discussed.

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AGGREGATED EMULSION OF HYDROCARBONS FORMED WITH PARTIALLY HYDROPHOBIZED CHITOSAN OLIGOMER

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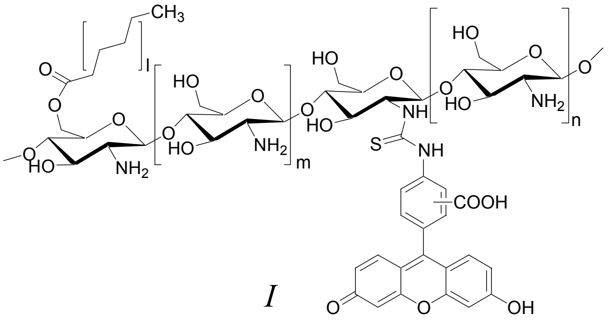
Water pollution with petroleum is hardly recovered in a short period because of difficult handling of adhesive and/or viscotic behavior of petroleum on water and harmful atmosphere over the polluted area[1]. Most of emulsifiers commercially available are still expensive and not easily biodegradable[2]. In this report we proposed a novel recovery procedure of petroleum through electrostatic aggregation of W/O emulsion droplets stabilized by coating with partially hydrophobized amphiphilic polymers of biological origin.

Chitosan is a linear polysaccharide that carries one amino group on every saccharide unit. Partially digested oligomeric chitosan shows a certain solubility in water at neutral or lower pH because of chain-chain repulsion between the positive charges on the protonated amino groups. In higher pH or at higher ionic strength the chitosan oligomer showed a tendency to form molecular assemblies with higher molecular weight, suggesting that the repulsive force between charged amino groups regulated the degree of aggregation of chitosan oligomers. We estimated the attractive interaction energy of chitosan oligomer to form self-assembly through determination of the degree of aggregation under the controlled repulsive force in water.



I

Fig. 1. Partially hydrophobized chitosan with fluorescein moieties (***I***, l = 4~6).

Partially modified chitosan oligomers with long alkyl chains (***I***) showed altered attractive interaction energy, possibly because of additional hydrophobic interaction between the alkyl chains. This result led us to establish a generally applicable method to determine hydrophobic interaction energy in partially hydrophobized polysaccharide self-assemblies.

Similar kind of polysaccharides such as cholesterol hydrophobized pullulan was shown to have an effective ability to cover the surface of liposomes[3] and oil droplets in w/o emulsion. Authors were inspired from Akiyoshi and Sunamoto's results[4] that the alkyl-hydrophobized chitosan (***I***, AHC) can form spontaneously whole coverage of oil droplets to be stabilized as emulsion in sea water. To provide a controlled hydrophobicity for effective coating ability on oil droplets, chitosan was modified with alkylacyl chloride in DMSO to give about one alkylacyl chain per 100 saccharide units. Water solubility of the modified chitosan derivatives reduced at neutral pH, but in acidic condition they showed fine solubility. These results encouraged authors to prepare further reinforced coating of oil droplets by building hydrogen bonding networks between polysaccharides after coating of oil droplets. Once it is emulsified, an easy removal of oil pollution will be achieved and then again hydrophilic polymer with anti-charge helps us to collect the stabilized oil droplets together resulting solid aggregates which is easily removed from environment. Microscopic observation of oil droplet stabilization and aggregation with negatively charged polymers will be shown. Effective and low cost removal of petroleum pollution in sea water will be discussed concerning with supramolecular assembly of natural polymers controlled by hydrophobic effect and electrostatic interactions.

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INNERMOLECULAR CARBENE REACTIONS WITHIN CYCLODEXTRINS

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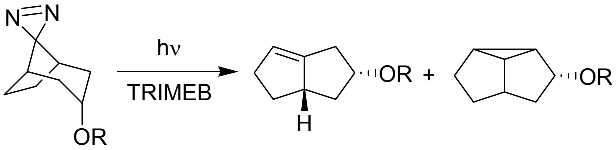
Our purpose is to alter the reactivity of a carbene and enhance the regioselectivity of its reactions. By complexation of the carbene precursor[1], the reactive species is confined in a restricted space and is severely limited to react indiscriminately. Since in some cases the carbene has been shown to react with the hydroxy groups of underivatized cyclodextrins[2], the reactions were also performed in trimethyl-β-cyclodextrin (TRIMEB). Complexes between a carbene precursor (diazirine) and a cyclodextrin [β-cyclodextrin ***(7-Cy)*** or TRIMEB] were prepared and analyzed by NMR and induced circular dichroism (ICD). The complexes were then irradiated in the solid state and in solution and the resulting products determined.

We found that *endo*-8-azibicyclo[3.2.1]octan-3-ol ***(1a)*** forms a 1:1 complex with both cyclodextrins investigated. ***1a@7-Cy*** has an association constant of 2340 M^{-1} in H_2O/MeOH 90/10. From 2D ROESY experiments it is obvious that the hydroxy group of ***1a*** is positioned at the wider rim of the cyclodextrin and that the diazirine group is not deeply immersed in the cavity. As it can be shown by ^1H NMR, ***1a*** produces also an inclusion complex with TRIMEB but this complex is weaker (K = 460 M^{-1} in H_2O). In the solid state (X-ray structure analysis), this complex is stabilized by a hydrogen bond between the guest and the oxygen atom of one of the glucosidic bonds of TRIMEB. The whole guest molecule lies above the plane defined by the glucosidic O(4) atoms. The observed competing reactions of diazirine ***1*** are the following: an alkyl migration to the bicyclo[3.3.0]octene ***2*** and a 1,3-C–H insertion to tricyclo[3.3.0.0^{2,8}]octane ***3***. We describe the first carbene reactions within a cyclodextrin that cannot lead to products resulting from an insertion into the O–H bonds of the host.



1 ***2*** ***3***

Scheme 1. Photolysis of ***1*** (***a***: R=H; ***b***: R=Me) .

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VIBRATIONAL CIRCULAR DICHROISM AND IR ABSORPTION STUDY OF DNA – PORPHYRIN COMPLEXES

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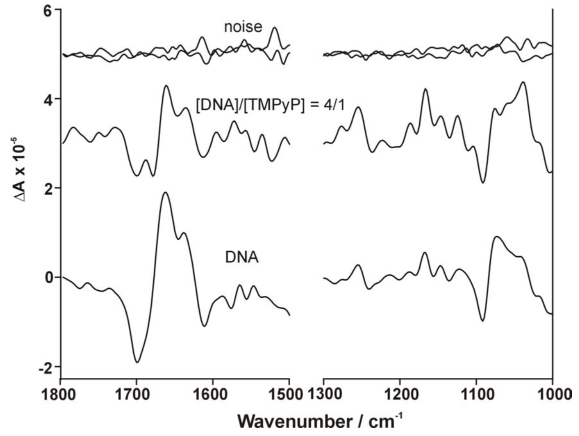
Meso-tetrakis(1-methyl-4-pyridyl)porphyrin (TMPyP) is utilized as a model system for the DNA binding anticancer drugs used in phodynamic therapy and in molecular biology applications. The porphyrin-DNA binding mechanisms that involve intercalation, external groove binding, and external binding with self-stacking of porphyrins are extensively studied[1].



The vibrational circular dichroism (VCD) and IR absorption study was performed for the [DNA]/[porhyrin] ratios in the range 2/1 – 10/1. The study was carried out in carbonyl and phosphate spectral regions in the D_2O and H_2O solvents, respectively.

After binding of TMPyP to DNA, the new bands at 1689 cm^{-1} and 1104 cm^{-1} were observed in VCD spectra. The first band was classified as a negative part of couplet assigned to C_6=O guanine, C_2=O cytosine, and C_4=O thymine stretchings and the second one as PO_2^- symmetric stretchings. On the basis of spectral changes observed we conclude that the most significant distortion occurred for GC base pairs due to intercalation and the external binding of porphyrin along the phosphate backbone chain also occurred.

The work was supported by the research grant of Ministry of Education, Youth and Sports of the Czech Republic (MSM 223400008)

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SPECTROSCOPIC STUDY OF INTERACTION OF DNA AND CHIRAL DISTAMYCIN DERIVATIVES

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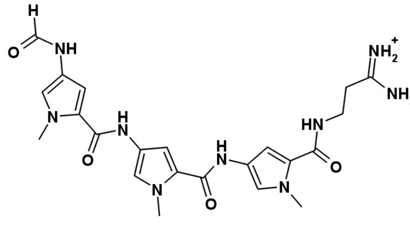
Distamycin A (***I***), the antitumor antibiotic, possesses the exclusive specificity and affinity to bind in the DNA minor groove rich in A – T nucleotide base pairs[1]. In order to study the interaction between both agents, the new derivatives of distamycin (***II)*** were synthesized. The Troeger's base was chosen as the chiral molecular spacer between two distamycin derivatives containing various number of pyrrol units. After synthesis, the distamycin derivatives exist as the racemic mixture.



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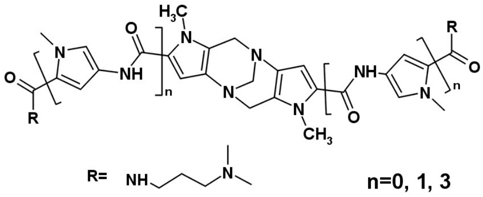

II

The interaction between distamycin derivatives and DNA was proved by the NMR and UV-vis study. The secondary structure of the biomacromolecular template, DNA, was observed by vibrational circular dichroism spectral patterns corresponding to C=O vibrations of the nucleotide bases (~1700 – 1650 cm^{-1}) and symmetric PO_2^- vibration (~1150 – 1000 cm^{-1}) of the sugar-phosphate backbone. The guest part of complex, distamycin derivative, was followed by electronic circular dichroism in UV spectral region. The dependence of interaction on the number of the pyrrol units contained in the distamycin derivatives was studied and discussed.

Grant MSM 223400008 from the Ministry of Education, Youth and Sports of the Czech Republic supported the work.

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SYNTHESIS OF OXATHIACROWN ETHERS – NEW HOSTS FOR TRANSITION AND HEAVY METALS AND STUDY OF THEIR FLUORESCENT AND EXTRACTION PROPERTIES.

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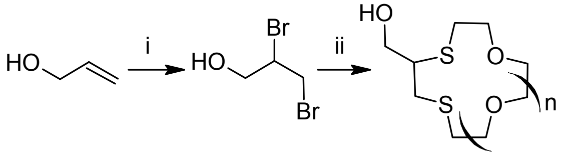
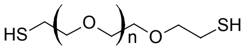
In this report we present a synthesis of 12- and 15-membered thiacrown ethers, possessing prospective fluorescent probes – prospective fluorescent sensors for transition and heavy metal ions.

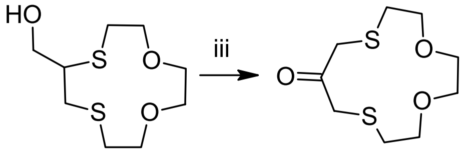
According to the procedure[1] for thiacrown ether, hydroxymethyl 12- and 15-membered oxathia-crown ether has been synthesized, starting 2,3-dibrompropyl alcohol ***1*** and α,ω-dimercaptanes ***2*** and ***3***, derivatives of tri- and tetraethylene glycol. Unlike the commercially available compound ***2***, the latter was obtained according to the literature.



1

4 n=1
5 n=2

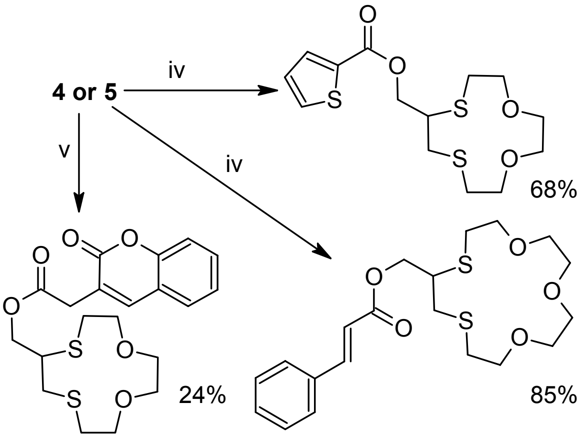
Scheme 1. (i) Br_2, $CHCl_3$, -20°C; (ii)  **2** (n=1) or **3** (n=2), Li_2CO_3, EtOH/H_2O, 95°C



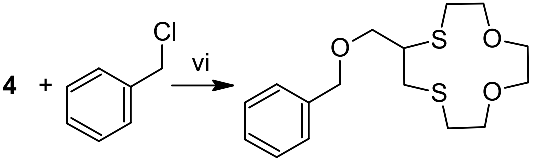
5 **6**

Scheme 2. (iii) 1. DMSO, $(ClCO)_2$, -78 – 20 °C, CH_2Cl_2; 2. **5**, 40%

Compound **4** was derivatized by a series of acids possessing fluorescent properties by means of DCC – 4-dimethylaminopyridine protocol.



Scheme 3. (iv) DCC, 4-DMAP, CH_2Cl_2, rt; 1h; (v) DCC, CH_2Cl_2, rt, 5 d



Scheme 4. (vi) NaH, DMF, overnight, 37%

Compounds **4** and **5** are known[2,3], but have been obtained by other means. Attempt to convert the oxymethyl group in **4** to aldehyde group failed, the use of Swern oxidation protocol lead to rearrangement, yielding to the known compound[4] **6**.

All new compounds were characterized by necessary spectral data and elemental analyses. Photochemical and extraction properties of some of these crown ethers are studied.

Support of INTAS (Grant N .4696), as well as support of the Department of Chemistry, Moscow State University, is gratefully acknowledged.

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HOST-GUEST COMPLEXES OF NATURAL AND MODIFIED CYCLODEXTRINS WITH NICOTINIC ACID

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Cyclodextrins (CD) are cyclic oligosaccharides composed of 6-8 glucose units. The actual and potential industrial applications of CDs in pharmaceuticals, foods, cosmetics, biochemistry, chemistry and technology are based on their ability to alter physical, chemical, and biological properties of guest molecules through the formation of inclusion complexes. Therefore, we have focused our attention to studying the complexation of natural and modified CDs with nicotinic acid. Nicotinic acid or niacin, the water-soluble B vitamin, has therapeutic action (for instance, prevents pellagra, lowers total cholesterol) and is required by our cells for the synthesis of co-enzymes.

In this work the thermodynamic parameters of complex formation of nicotinic acid with α-CD, β-CD, and their hydroxypropyl-derivatives and monomer units (glucose and maltose) in aqueous solutions have been obtained at 298.15 K and various pH by calorimetry of solution and UV-spectrophotometry. ^1H NMR spectroscopy has been employed to confirm the inclusion of guest molecule into CD's cavity and to determine the stoichiometry of the complexes (Job's method).

It was found, that interaction of CDs with nicotinic acid is selective. Only α-CD and hydroxypropyl-α-CD form 1:1

inclusion complexes with nicotinic acid. The influence of different factors (such as structure of solutes, dimensions of CD's cavity, availability of substitutes in CD's molecule, pH) on the thermodynamic parameters of complexation is analyzed.

This work was supported by the grant of Russian Foundation of Basic Research (№03-03-96411) and the Grant of President of Russian Federation for young scientists (MK 1060.2003.03).

SURFACE-ENHANCED RAMAN SCATTERING SPECTROSCOPY. STUDY OF SUPRAMOLECULAR COMPLEXES OF CROWN-ETHER CONTAINED PHOTOCHROMIC IONOPHORES IN ORGANIC SOLVENTS

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Surface-enhanced Raman scattering (SERS) spectroscopy is a vibrational spectroscopy technique, which has highly increased selectivity and sensitivity as compared with conventional Raman and IR spectroscopy. It operates due to SERS-active substrate, which enhances Raman scattering from the adsorbed molecules. This technique is a recognized tool for investigation of molecules and their complexes in aqueous solutions. Degradation of SERS-active substrates in organic solvents restricts SERS spectroscopy applicability to the study of the molecules, which are soluble or possess unique properties in organic solutions only. We were able to resolve this problem, and now we are widely using SERS spectroscopy for investigation of molecular complexes of crown-ether contained photochromic ionophores. In this report, we describe preparation of the SERS-active substrates, which are stable at least in methanol, ethanol, trifluoroethanol and acetonitrile. We review the range of possible applications of SERS spectroscopy with the results of the following studies: investigation of charge transfer mechanism between bis-crown ether stilbene and bisammonium derivatives of dipyridylethylene[1]; study of complexation of metal cations with crown-containing spironaphthoxazine[2], 3,3-diphenyl-3H-benzo[f]chromene[3], styryl[4] and butadienyl[5] dyes.

This work was supported by INTAS grant.

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STEREOSELECTIVE SYNTHESIS OF TRIPHENYLENE KETALS USING METAL TEMPLATES

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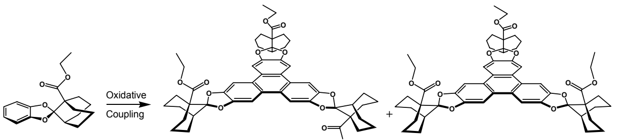
Triphenylene ketals are novel C_3-symmetric scaffolds with nano-scale dimensions[1]. With appropriate affinity groups the first artificial caffeine receptor has been established[2]. Chirally-modified derivatives are capable of enantiofacial differentiation of single heterocyclic substrates[3]. The preparation of these valuable scaffolds is usually achieved by oxidative coupling of the corresponding catechol ketals employing $MoCl_5$. For large-scale preparations an anodic protocol was developed[4]. In all procedures the statistical mixture of all-*syn* and *anti*,*anti*,*syn* derivatives is obtained.



Scheme 1. Oxidative coupling of catechol ketals

Unfortunately, the desired all-*syn* isomer is only formed as the minor component. Furthermore, using covalently bound templates on the catechol ketals did not succeed[5]. The potential of the $MoCl_5$-mediated coupling reaction could be enhanced by employing Lewis acidic additives[6]. Surprisingly, application of these reaction conditions totally reversed the result of the oxidative trimerization. In contrast to the statistics the all-*syn* derivative is strongly preferred, creating a synthetically very attractive pathway. In order to explain the selectivity, a multinuclear template has to be anticipated. The scope of the transformation will be outlined in detail[7].

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SYNTHESIS AND PROPERTIES OF ARTIFICIAL CAFFEINE RECEPTORS

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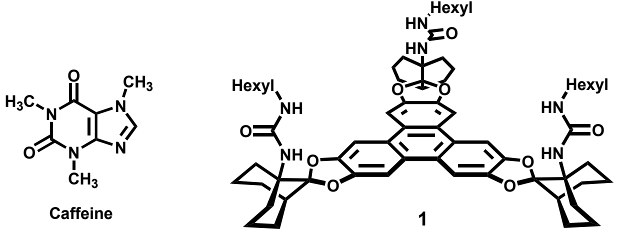
Caffeine is among the most frequently consumed alkaloidal compounds and is omnipresent in many plants. The traditional significant sources of caffeine in daily life are coffee, black tea and cocoa. Actually, the alkaloid is also an ingredient of Cola beverages and energy drinks. Many analgesics sold over the counter contain also caffeine. Because of the wide range of applications and the potential of new analytical tools, caffeine is currently gathering an increasing attention[1].

Recently, we reported the synthesis of functionalized triphenylene ketals which represent the rigid C3v symmetric scaffold of our novel receptor (**1**). The cleft-like structure exhibits a high affinity to caffeine and does not interfere with the alkyl groups of the oxopurine system leading to a novel concept for the molecular recognition of caffeine and related compounds[2].



Scheme 1.

Here, the synthesis and properties of these caffeine binding systems will be outlined, which led also to a chiral modification of the caffeine receptor and the first colorimetric assay for caffeine[3].

The construction of the receptor scaffolds required the development of novel synthetic methodologies. The potential of $MoCl_5$-mediated and anodic protocols for the oxidative aryl-aryl-coupling will be discussed briefly[4].

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TWO FACES IN A COMPLEX: ASSESSMENT OF ENANTIOFACIAL DISCRIMINATION ON HETEROCYCLES BY CHIROOPTICAL TOOLS

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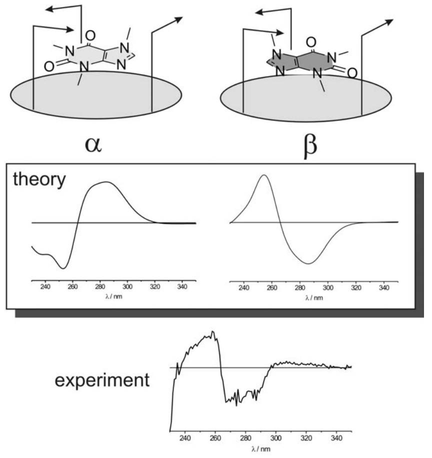
The reversible enantiofacial discrimination on extended heterocyclic moieties is a challenge for supramolecular chemistry. After development of the first artificial caffeine receptor[1] various chirally modified systems were synthesized aiming for this goal[2].

Based on steric interactions, these systems are able to distinguish between the two enantiotopic faces of various prochiral guest molecules. The assignment of the face selectivity was up to now exclusively possible by X-ray analysis. Thus, we developed a faster and more convenient approach based on CD spectroscopy to assert the enantiofacial preference in solution.



The calculation of the spectra involved a combination of Molecular Dynamics and quantum-chemical calculations used for the first time for non-covalently bound systems[3]. The simulated spectra are in good agreement with the experiments and the absolute configuration of various host-guest complexes was determined[4].

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ORGANOFUNCTIONAL METAL OXIDE CLUSTERS AS BUILDING BLOCKS FOR INORGANIC-ORGANIC HYBRID POLYMERS

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Various (meth)acrylate-substituted metal oxide/alkoxide clusters of the general formula $M_xO_y(OH)_u(OR)_v(OOCR)_w$ (M = Ti, Zr, Hf, Ta, Ti/Zr, Ti/Hf) with various compositions, structures, diameters and shapes can be obtained by reacting metal alkoxides with (meth)acrylic acid[1]. The type of obtained cluster depends mainly on the metal alkoxide/carboxylic acid ratio and the kind of alkoxide groups of the parent metal alkoxide. The method is based on a self-limiting assembly of molecular building blocks and the in-situ generation of water by ester formation. The clusters differ by the mutual connection of the metal polyhedra. In each case, the metal oxide cluster core – with dimensions between 0.7 and 1.8 nm – is capped by the (meth)acrylate ligands, which are fully accessible for polymerization reactions.

Radical polymerization of small proportions of the clusters (0.5 – 2 mol%) with unsaturated organic co-monomers (methylmethacrylate, acrylic acid, styrene, etc.) results in inorganic-organic hybrid polymers in which the clusters crosslink the polymer chains[2]. Glassy materials were typically obtained upon copolymerization of the clusters with MMA, while copolymerization with MA resulted in insoluble powders with high specific surface areas. EXAFS and SAXS measurement showed that the structural integrity of the clusters is preserved upon polymerization. Depending on the cluster type, either a statistical distribution of the clusters in the polymer or some aggregation was observed[3].

The swelling behavior in organic solvents, the thermal stability, the dielectric properties and the mechanical properties of the polymers are distinctly changed by incorporation of the functionalized clusters. The properties depend on the cluster portion in the polymer and also – to some extent – on the kind of cluster[4].

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FUNCTIONALISED CALIX[n]ARENES INVOLVED IN MOLECULAR RECOGNITION OF AMINO ACIDS

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Calix[*n*]arenes as synthetic macrocyclic receptors are intensively involved in studying the characteristic interactions presented in host-guest recognition[1-3]. Their ability to encapsulate the biological compounds such as amines, amino acids or peptides recommends them as biomimetic receptors for separation processes[4-6].

In this work we have studied aspects of complex formation, solvent extraction, and transport through liquid membrane of amino acids by calix[n]arene derivatives. The complexation properties of calix[n[arenes towards amino acids were evaluated by calorimetric titration and UV-vis spectroscopy.

The interactions established between calixarenes and these compounds are of current interest in the understanding of specific biomolecular interactions. The effects of physicochemical parameters that might influence the separation of amino acids by extraction process, and the transport through liquid membranes using the calix[n]arenes as carriers have been investigated.

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MODIFICATION OF METALCONTAINING NANOPARTICLES, ENCAPSULATED INSIDE THE POLYMERIC MATRIXES BY THE DIRECTED CHEMICAL REACTIONS

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In our days there is a problem of obtaining nanoparticles of fixed composition with fine-bored sizes distribution, that, for the objective reasons, is not always given possible. For the decision of a task in view the method of chemical modification obtained nanoparticles inside a polymeric matrix was developed. The essence of a method consist in selection of such chemical reactions and conditions of their carrying out which would allow to transform nanoparticles with one composition to nanoparticles with other composition without change of their sizes and distribution inside a polymeric matrix. In this work the opportunity of modification nanoparticles of iron, copper, their oxides and chlorides with the gaseous Cl_2 and HCl, and also reducers was investigated. One of stages in this work was obtaining nanoparticles with composition of Bi_2O_3 (α - and β - modifications) by direct synthesis, and the directed oxidation from metal bismuth nanoparticles.

Obtaining metalcontaining nanoparticles was carried out by a method of high-speed thermal decomposition corresponding precursors in a solution - melt polyethylene (PE)-oil at temperatures about 270-330 °C. The temperature was selected specially for everyone precursor according to their thermal decomposition temperature. All obtained materials was characterized by methods TEM, XRD and EXAFS. It is shown, that after processing materials with reducers, and also gaseous Cl_2 and HCl the size of metalcontaining nanoparticles does not increase. For example, for ferruginous nanoparticles before reaction particle size was about 4 – 4.5 nanometers. TEM-microphotograph typical for ferruginous nanoparticles show on Fig. 1. Ferruginous nanoparticles also were investigated with the method Mossbauer spectroscopy. Reactions with participation of gaseous Cl_2 and HCl, and also reduction and oxidation were spent with obtained nanoparticles.

It is shown, that obtained nanoparticles encapsulated inside a polymeric matrix have high reactivity. During performance of work was indicated, that chlorides of corresponding metals (II) are obtained at influence on composition nanomaterials by gaseous chlorine, and also hydrochlorine. These chlorides can yield oxychlorides by interaction with air. Formation metal nanoparticles was observed reduction of materials containing Cu and Bi oxides nanoparticles on air, and in case of ferruginous nanoparticles at the same time with a metal phase within several minutes "protective" shell Fe_2O_3 was formed. At carrying out of similar reaction in an inert atmosphere in all samples only the metal phase was found out.

The spent researches have shown an opportunity of modification metalcontaining nanoparticles, stabilized in volume of the polymeric matrixes by the directed chemical reactions.

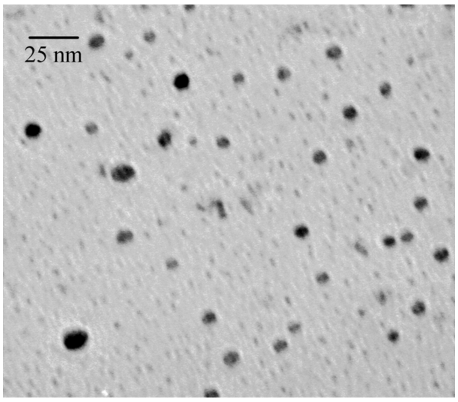

Fig.1. TEM-microphotograph of 10 % Fe_3O_4 containing nanoparticles inside the PE matrix after modification by gaseous Cl_2.

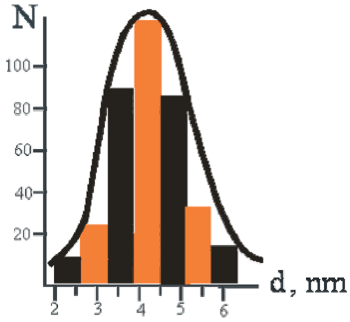

Fig.2. Size distribution of nanoparticles presents on the preview TEM image. Middle size ~ 4.2 ± 1,0 nm.

This work was supported by the Russian Foundation for Basic Research (grant nos. 02-03-32435, 04-03-32090, 04-03-32311, 04-03-32597), the International Science and Technology Center (project no. 1991), "Russian Science Support Foundation" and the Russian Academy of Sciences through the basic research program "Critical Issues in the Physics and Chemistry of Nanoscale Systems and Nanomaterials".

NEW COORDINATION MODE OF PENTAPYRIDYLTETRAMINE: CRYSTAL STRUCTURES OF $[Ni_3(H_2peptea)_2](CF_3SO_3)_2$ AND $[Ni_3(dpa)_2(H_2peptea)(CH_3CN)](ClO_4)_2$

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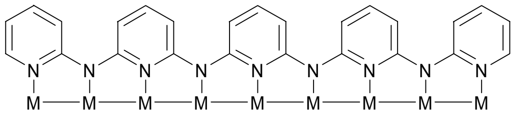
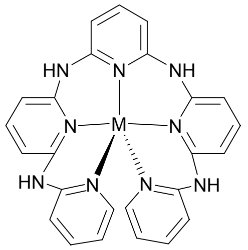
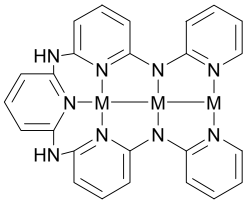
The coordination chemistry of oligo-α-pyridylamino ligands has been an interesting topic. The specific conformations and chemical properties of these complexes are particularly concerned[1-3]. These linear multinuclear metal string complexes have the potential as molecular metal-wires and can act as the building blocks to form the one-, two-, or even three-dimensional polymeric compounds. Some one-dimensional coordination polymers have been achieved in which the trinickel metal string complexes are linked by the different axial ligands as a bridging ligand or forming hydrogen bonding[4]. In our previous reports, the H_4peptea [H_4peptea = pentapyridyl-tetramine] ligand can bind metal ions with two conformations, the all *syn*-form[3] and the all-*anti* form[1]. Here, we report the new coordination mode of H_4peptea, *syn-syn-anti-anti-anti-anti-syn-syn* form.



Form (all-*syn*)





Form (all-*anti*) Form (*syn-syn-anti-anti-anti-anti-syn-syn*)

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DNA STRUCTURE VARIATION STUDIED BY VIBRATIONAL CIRCULAR DICHROISM SPECTROSCOPY

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Since the first vibrational circular dichroism (VCD) study on nucleic acids[1], the attention has been focused on two spectral regions. In the first one, the base-stretching modes (C=O, C=N, and C=C) are manifested, in the second one the PO_2^- stretching and sugar modes are observed.

In present study, the physicochemical conditions (pH, the ionic strength, and temperature) in the calf thymus DNA solutions were varied and the spectral response in VCD and IR absorption spectra were observed. Utilizing the both spectral regions, the structural changes of the base sidebands and sugar-phosphate backbone of DNA can be observed separately.

The effect of the pH variation observed in the both spectral regions is demonstrated in the Fig. 1. In the base-stretching region, the pH decrease towards acidic values causes the gradual decreasing of the VCD signal, the increase of pH towards alkali values causes the complete diminishing of the VCD signal of DNA. However, in the phosphate region, the spectra possess the VCD signal even at extreme pH values.

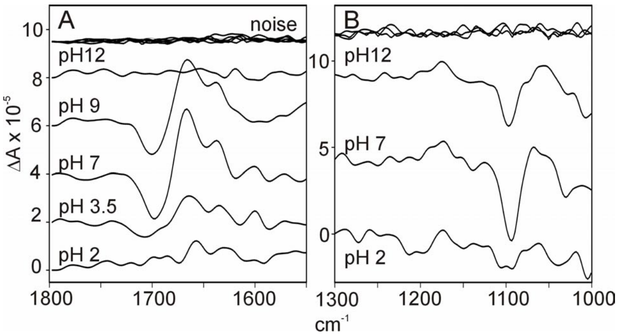

Fig. 1. VCD spectra of the DNA solution in the base-stretching (A) and phosphate (B) regions.

The structural consequences of the VCD observations are discussed.

Grant MSM 223400008 from the Ministry of Education, Youth and Sports of the Czech Republic supported the work.

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INDUCED COTTON EFFECTS AS MANIFESTATION OF SUPRAMOLECULAR INTERACTIONS

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Contrary to the conventional organic chemistry concept, chirality can be generated by the interaction of associated molecules. The handed property of assembled molecules manifested by chiroptical spectra is due either to the formation of chiral conformers[1], or to the alignment of neighboring molecules held together by secondary chemical forces[2]. This talk deals with three types of supramolecular interactions: a) spontaneous self-assembly of carotenoids; b) the accommodation of ligands to protein binding sites; c) self-assembly formation on a template.

a) Carotenoids (hydroxyl-containing carotene derivatives) are soluble in water-miscible organic solvents but insoluble in water. When a solution in ethanol is diluted with water, the individual molecules associate and the structure of the self-assembly is strongly influenced by the number and position[3], as well as the configuration[4] of the hydroxyl groups. Owing to the supramolecular organization, highly intensive exciton couplets appear in the circular dichroism spectrum and characterize both card-pack and head-to-tail types of aggregates formed.

b) Proteins favor a definite shape of their ligands. Hence, achiral molecules often become chiral upon binding due to the adoption of chiral conformations recognized by the binding sites. Consequently, induced CD spectra are informative on the bound molecules. This technique could be utilized to characterize binding sites of human serum albumin[5,6], bovine lactoglobulin[7], and human α_1–acid glycoprotein[8].

c) In cases when multiple binding to a protein occurs, exciton signals may appear that the ligand molecules are located in a chiral array[8,9]. A rare example is presented when the docking of the first ligand molecule to human serum albumin induces subsequent formation of ligand assembly that is governed by the protein template[10].

In conclusion, the biological relevance of carotenoid self-assembly in nature is indicated and its utility as exciton probe is summarized.

The 1/047 NKFP MediChem national project and the QLKT-CT-2002-90436 EU project for Center of Excellence in Biomolecular Chemistry are acknowledged for financial support.

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LATE TRANSITION METAL CATALYZED CYCLIC OLEFIN COPOLYMERIZATION

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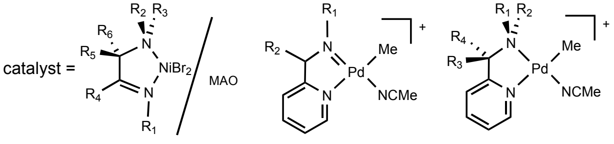
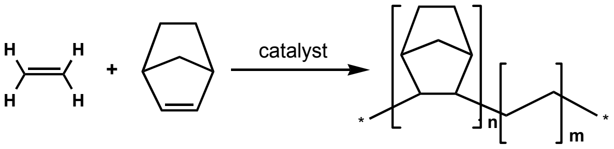
The late transition-metal catalysts bearing the designed ligands in constrained geometry used for olefin polymerization are acquiring increasing attention. Such catalysts not only demonstrate promising activity, but also confer the catalytic reactions as well as the polymeric products with characteristic properties, particularly different from those caused by the early transition-metal catalysts.

On the other hand, seeking for the bidentates that contain hybrid coordinating functionalities remains a rising field since the study of the SHOP process. It is generally believed that the dissymmetrical ligands potentially enable to afford more controlling features to the reactivity.

We will report the nickel catalysts bearing new amine-imine bidentate ligands (type I) as well as the organopalladium catalysts bearing imino-pyridine or amino-pyridine ligand (types II & III). Such catalysts exhibit high reactivity (10^3 Kg·metal $mol^{-1}\cdot h^{-1}$) for the copolymerization of ethylene and norborylene. For catalysts I, the use of MAO as co-catalysts is required.



I II III



In contrast to the mCOCs, the products of cyclic olefinic copolymers resulting from the late transition metals contain high percentage of noynorlene fragments, thus high T_g, but still soluble in nonpolar organic solvents. The values of M_n may be several thoughsand using catalysts I to 10^5 using catalysts III with PDI generally less than 2. The detailed catalytic data and the ligand correlation will be discussed.

FORMATION OF THERMODYNAMICALLY AND KINETICALLY STABLE COMPLEXES IN WATER WITH A TETRAANIONIC HOST

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We have developed a water soluble molecular receptor which binds guests in a thermodynamically and kinetically stable fashion. This cavitand-based host is composed of a preorganized aromatic pocket whose upper rim is composed of four carboxylate groups (Fig. 1). The resulting host-guest complexes have been characterized by ^{1}H NMR and isothermal titration calorimetry (ITC).

Guests for this system include tetraalkyl ammonium salts and hydrocarbons of the appropriate size and shape. Guest binding behavior has been studied in response to changes in buffer identity, salt concentration and pH. This host can also function under physiological conditions in the presence of SDS micelles.

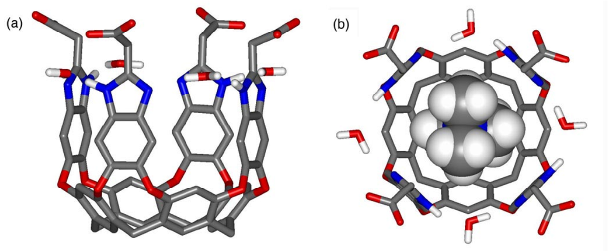

Fig. 1. (a) Side view of host; (b) Top view of host in the presence of a tetraalkyl ammonium guest.

The authors would like to thank The Skaggs Institute for Chemical Biology, the NIH (GM 27932), and the Deutsche Forschungsgemeinschaft (E.C.U.) for financial support. We also thank Dr. Laura Pasternak (TSRI) for NMR assistance and Prof. Pablo Ballester (Universistat de les Illes Balears, Spain) for helpful discussions.

SUBSTITUTED BICYCLO[1.1.1]PENTANES FOR MOLECULAR AND SUPRAMOLECULAR CONSTRUCTION SET

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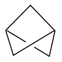
Construction of giant molecular or supramolecular objects in contemporary supramolecular chemistry frequently uses smaller molecular modules of well-defined geometry and functionality, which predetermine structure and properties of resulting assemblies. A number of structural patterns have already been used in synthesis of such modules including some very sophisticated. Bicyclo[1.1.1]pentane cage ***1*** is one of them.



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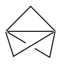

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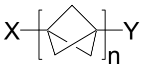
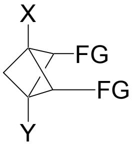


[n]***2***

Bridgehead-substituted bicyclo[1.1.1]pentanes became readily accessible after Szeimies' discovery[1] of a simple synthesis of their perfect precursor, [1.1.1]propellane ***2*** and attracted soon the attention of synthetic chemists as a promising building blocks of molecular rods, [*n*]staffanes [*n*]***2***, offering small length increment (~3.5 Å) and interesting energy and electron transfer properties[2]. A number of such molecular rods has been synthesized so far with large selection of terminal functionalities. The synthesis of higher staffanes (n>3) as well as the synthesis of rods with odd number of bicyclopentane cages starves, however, from low yields (for recent review see[3]). Therefore, new more effective methods of [n]staffane preparation are of unceasing interest.

We are introducing a new structural pattern **3** based on highly strained bicylo[1.1.1]pentane cage, which benefits from placing additional functionalities (FG) on its bridge positions. The new substituents are on two parallel bonds in positions 2 and 4, perpendicular to 1-3 axis of the cage. Such configuration enables interaction of the functionalities in an "equatorial" plane of the cage defined by its rotation around the 1-3 axis. If used in staffanes, these functionalities (polarizable, electron donating or accepting, ionizable, *etc.*) can propagate the interaction along the light of such molecular rod.



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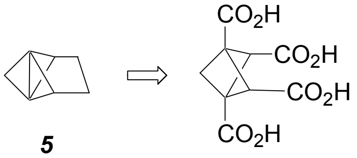

5 ***4***

Bicyclo[1.1.1]pentane-1,2,3,4-tetracarboxylic acid, that was suggested as a precursor of ***3***, was synthesized from tetracycloheptane ***5*** (ref.[4]). Chemoselective transformations of bridgehead and bridge carboxyls together with well-known synthetic potential of carboxylic functionalities open the way to building modules of required properties.

Financial support from Ministry of Education, Youth and Sports of the Czech Republic and National Science Foundation, U.S.A (project KONTAKT ME571) is acknowledged with thanks.

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APPLICATION OF TIO$_2$ PHOTOCATALYTIC NANOPARTICLES IN WATER SCRUBBER TO REMOVE VOLATILE ORGANIC COMPOUNDS

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Conventional water scrubber was modified by introducing TiO_2 nanoparticles to improve the efficiency of scrubber in removing both hydrophobic and hydrophilic contaminated gases. On the surface of well-dispersed TiO_2 nanoparticles, toxic organic materials are degraded into non-toxic minerals by photocatalytic degradation process (Fig. 1).

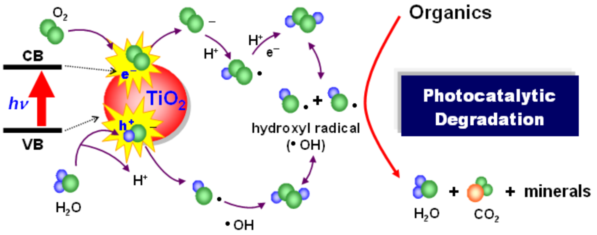

Fig. 1. Schematic representation of mechanism of photocatalytic degradation process of TiO_2 nanoparticle.

Several commercial TiO_2 particles were characterized using various methods: X-ray diffraction (XRD) to determine crystal structures, dynamic light scattering (DLS) to measure particle size, Brunauer-Emmett-Teller (BET) analysis to measure total surface area. The chosen as photocatalyst of present study has 100% anatase crystal structure, 3-120 nm of particle size, and 60 - 450 m^2/g of surface area.

The batch type scrubber with TiO_2 photocatalyst was designed in a lab scale, and used to characterize the performance in removing highly concentrated contaminated gases. The mechanism of photocatalytic degradation in photocatalytic scrubber was characterized using gas chromatography (GC). The removal efficiency of hydrophilic gases such as ammonia, acetic acid and hydrophobic gases such as octanol, toluene was much higher than that of conventional water scrubber. The gas chromatography equipped with mass spectrometry (GC-Mass) was also used to determine the intermediate gases during photocatalytic degradation. From these results, it was confirmed that the high efficiency of modified lab scale scrubber in removing the contaminated gases was caused by TiO_2 photocatalytic process.

The continuous type scrubber with TiO_2 photocatalyst was designed in a pilot plant scale, and used to confirm the applicability in a removal of low concentration contaminated gases. The removal efficiency of both conventional water scrubber and modified pilot scale photocatalytic scrubber was characterized using ultra violet–visible spectrophotometry (UV-vis) instead of GC and GC-Mass due to low signal intensity. The removal of removed hydrophilic gases such as acetic acid and hydrophobic gases such as toluene and benzene using lab scale photocatalytic scrubber was found to be very effective, while that of conventional water scrubber was inferior.

It is concluded that the modification of conventional water scrubber using TiO_2 photocatalytic process is one of powerful alternatives having improved efficiency in removing both hydrophobic and hydrophilic contaminated gases.

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WATER SOLUBLE GREEN PERYLENEDIIMIDE DYES AS POTENTIAL SENSITIZERS FOR PHOTODYNAMIC THERAPY

FUNDA YUKRUK and ENGIN U. AKKAYA*

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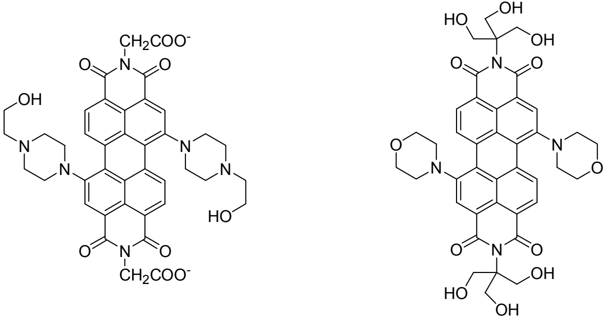
Photodynamic therapy has been established as one of the approaches for the treatment of various malignant tumors. While most of the reagents used for this purpose are porphyrin derivatives, there is a strong motivation for finding novel and better sensitizers. Perylenediimides are known for their photo- and chemical stability, but they do not have absorptions in the red end of the visible spectrum. However, recently reported[1-3] green perylenediimides which have dialkylamino substituents on the perylene core, may provide an alternative. To that end, we have designed and synthesized novel green perylenediimides with remarkable water solubility at neutral pH and absorption peaks beyond 650 nm.



1 2

Scheme 1. Two examples of the green perylenediimides synthesized and investigated in this study.

We also demonstrated that on red-light excitation, singlet oxygen trap 1,3-diphenylisobenzofuran is rapidly degraded. While cell culture studies in our labs is in progress, we are hopeful that we have the first examples of perylenedimide class singlet oxygen generators for use in photodynamic therapy.

Authors gratefully acknowledge support form the METU Research Fund.

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ARTIFICIAL HYDROLYTIC METALLOENZYME MIMICS BASED ON A XANTHENE FRAMEWORK

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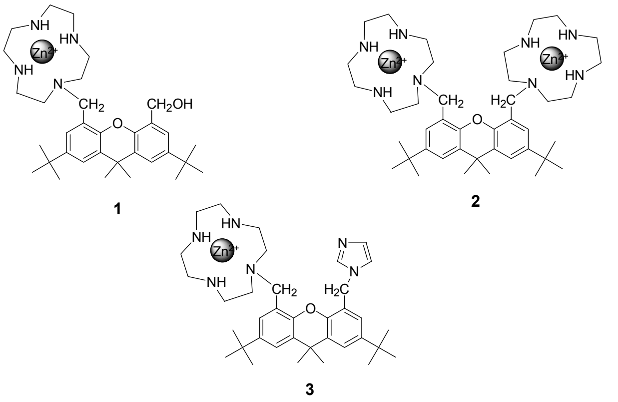
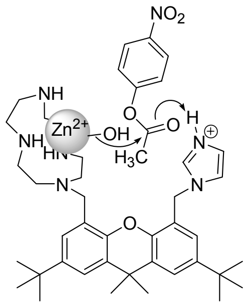
Artificial enzyme design is an active field of supramolecular chemistry[1]. Metalloenzymes are attractive targets in such studies, because in these enzymes active sites feature metal ions, and the hydrolytic activity of these complexed ions can be relatively easily approximated in model systems. Many hydrolytic enzymes carry one or more metal centers, and in most cases there is a cooperativity between the metal centers[2]. However, in enzymes, there are always additional interactions; in fact, enzymatic catalysis is essentially a 'multifuctional' catalysis.

In order to investigate effectiveness of bifunctional enzyme mimics, in comparison to the binuclear and mononuclear metalloenzyme models, we have designed and synthesized three novel enzyme models (**1**-**3**). Using the model substrate *p*-nitrophenyl acetate, we showed that the bifunctional model (**3**) is at least an order of magnitude more active in catalyzing the hydrolysis of the substrate.



Scheme 1. Zinc(II) complexes of the three ligand synthesized in this study.

Compared to the uncatalyzed hydrolysis reaction of the *p*-nitrophenyl ester at pH 7.0, the model complex **3** showed a 5700-fold rate acceleration. The proposed mechanism of hydrolytic activity in the bifunctional enzyme mimic is as follows:



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VIBRATIONAL CIRCULAR DICHROISM SPECTROSCOPY AS A TOOL TO STUDy SUPRAMOLECULAR SELF-ASSEMBLY

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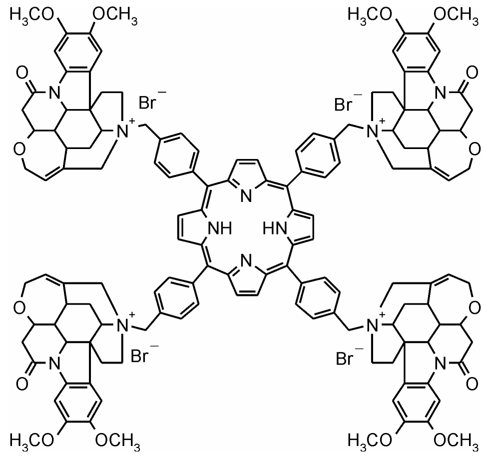

Scheme 1. Molecular structure of brucin-appended conjugate studied.

Characterization of the self-assemblies[1] is accomplished by numerous methods, mainly by NMR, IR, Raman, and fluorescence spectroscopy, scanning and transmission microscopy. Among the self-assembled species, the chiral molecules play an important role. In addition, the optical activity of originally achiral molecule can be induced by spatial arrangement during the self-assembly. Therefore, the chiroptical technique, electronic circular dichroism (ECD) spectroscopy, has been utilized to observe the self-assembly of chiral molecules. Herein we report the use of another chiroptical method, vibrational circular dichroism (VCD) spectroscopy.

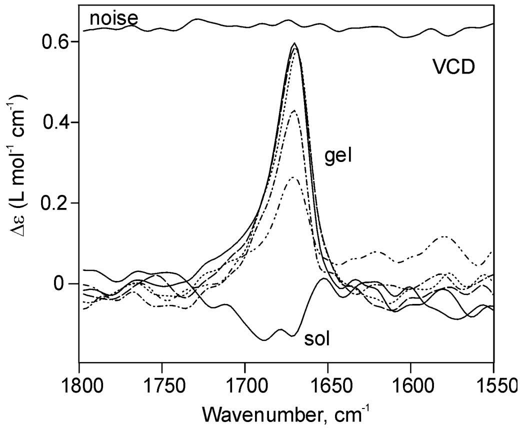

Fig. 1. VCD spectra of gel (positive peak) and sol (negative peak) phases of brucin-appended porphyrin gelator. The gel-sol transition is caused by the temperature variation from 20 to 70°C.

We consider the VCD technique as a beneficial tool of the self-assembly study for the following reasons: (i) VCD is intrinsically sensitive to stereochemistry of chiral compounds. (ii) The stereochemical information obtained is related to the group of atoms, which participate in characteristic vibration observed as particular spectral band. (iii) Structural features are obtained for chiral small as well as large molecules and their complexes and conjugates. (iv) Influence of the physico-chemical condition variations on self-assembly process can be followed by the VCD technique.

The first example, where the VCD technique was employed in the study of self-assembly, is the study of sol-gel phase transition of tetrabrucine-porphyrin conjugate (Scheme 1). The gel-to-sol transition caused by the temperature increase is demonstrated by the sign change of the VCD signal of the C=O stretching (Fig. 1). Therefore, the C=O groups were identified as the molecular sites whose spatial structure is changed during the sol-gel transition[2].

As the second example, the self-assembly study of biaryl derivative is presented. In the DMSO solution, where the aggregation is prevented, a weak positive VCD couplet is observed in carbonyl region. In the $CDCl_3$ solution, a negative couplet of about twenty times higher intensity is observed in the same region (Fig. 2). VCD spectroscopy proved to be very sensitive method not only for the self-assembly detection but also for identification of the groups involved in the noncovalent interactions.

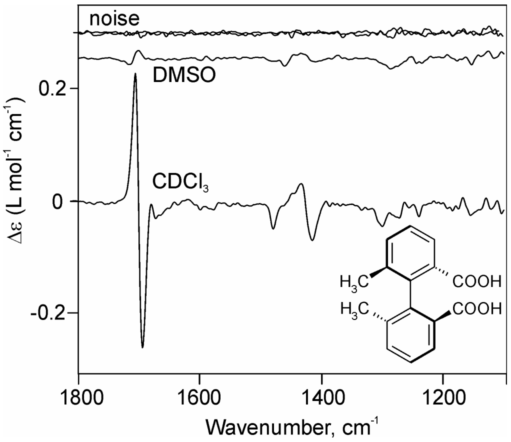

Fig. 2. VCD spectra of the biaryl derivative solution in DMSO and in $CDCl_3$.

Grants MSM 223400008 and 1K03012 from the Ministry of Education, Youth and Sports of the Czech Republic supported the work

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CHIRALITY INDUCTION OF π-CONJUGATED POLYMER OR MOLECULE THROUGH CONJUGATED COMPLEX FORMATION

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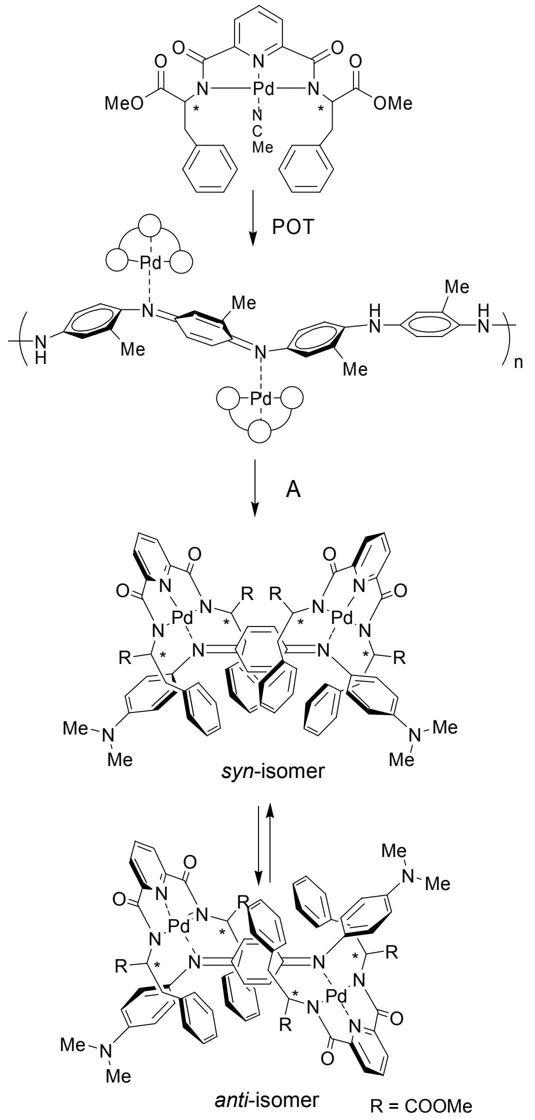
Polyanilines are one of the promising electrically conducting polymers with chemical stability. In recent year, there has been increased interest in chiral induction of polyanilines because of their potential use in diverse areas such as surface modified electrodes, molecular recognition, and chiral separation. Chiral polyaniline has been reported to be formed only by the chiral acid dopant[1]. In our previous papers, complexation of polyanilines or the oligomer with transition metals modulates the redox properties of the quinonediimine unit, which is related to the catalytic function in the oxidation reaction[2]. Furthermore, the controlled complexation with palladium(II) compounds has been achieved to afford the supramolecular cross-linked network or single-strand conjugated complexes, in which the quinonediimine moieties serve as bridging coordination sites[3].



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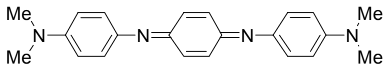

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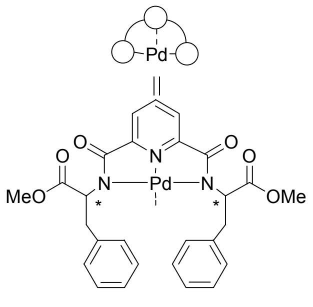

Use of chiral complexes is envisioned to induce chirality to a π-conjugated backbone, giving the chiral d,π-conjugated complexes. In this context, we herein report a new method for chirality induction of polyaniline derivatives.

Chirality induction of π-conjugated polyaniline derivative POT, poly(*o*-toluidine), was achieved by chiral complexation with chiral palladium(II) compounds as illustrated below.

The crystal structure of the chiral conjugated complex with a model compound of the polyaniline, *N*,*N*-bis(4'-dimethylaminophenyl)-1,4-benzoquinonediimine, revealed a chiral propeller twist conformation of the π-conjugated moiety.

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BIOCOMPATIBLE NANOPOLYMERS OF 3-HYDROXYBUTYRIC ACID VIA RING OPENING REACTION OF β-BUTYROLACTONE

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Anionic polymerization is generally known as a method of synthesis of well-defined tailor-made polymers[1] useful as drug delivery systems[2]. In our investigations ring-opening anionic polymerization of [*R*,*S*]-β-butyrolactone initiated with 3-hydroxybutyric acid sodium salt was chosen as the method of synthesis of oligo-3-hydroxybutyrates.

In order to study the effect of oligo-3-hydroxybutyrates on cell growth we performed the MTT-based drug resistance assay and clonogenic survival assay using transformed hamster fibroblasts cells (V79 line) and murine melanoma cells (B16 line). We have shown that [*R*,*S*]-3-hydroxybutyric oligomers are non-toxic and biocompatible, and can potentially serve as carriers able to vectorise drugs in the form of chemical conjugates for drug delivery. The methods of oligo-3-hydroxybutyrates preparation elaborated by us are simple and drug sensivity tests proved that these oligomers are non-toxic[3] and can be used in medical applications.

EC grant number G5RD-CT-2000-00294 and Polish grant number PBZ-KBN-082/T08/02

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NOVEL SUPRAMOLECULAR SYNTHESES OF NANO-BIOPOLYMERS AND THEIR APPLICATIONS IN DRUG DELIVERY SYSTEMS

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Using supramolecular catalysis based on two-electron transfer mechanism[1,2] and application of polar solvents[3,4] we are able to produce tailor made nanopolymers containing 3 up to 10 monomeric units of *R* or *R*,*S*-hydroxybutyric acid. These novel nano-polymers are biocompatible and nonotoxic[3]. Due to their excellent properties these novel nanopolymers can be used as drug vectors of anticancer drugs in chemotherapy.

Same syntheses of such drug-nanopolymer conjugates using anthracycline antibiotics as doxorubicin and its derivatives as well as some nonsteroidal anti-inflammatory drugs will be presented. The in vitro results using these drug-nanoconjugates are very promising and in vivo experiments are in progress. Using confocal laser scanning microscopy (CLSM) targeting and distribution of anthracycline drugs and their conjugates in cells cytoplasma and nuclei was found to be different[5].

Acknowledgement to EC grant number G5RD-CT-2000-00294 and Polish grant number PBZ-KBN-082/T08/02

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HOMOCHIRAL HYDROGEN-BONDED POROUS GRIDS IN THE CRYSTAL STRUCTURE OF RACEMIC BINAPHTHALENE-2,2´,6,6´-TETRACARBOXYLIC ACID. UNIQUE CASE OF ENANTIODIFFERENTIATION BY GRID CATENATION

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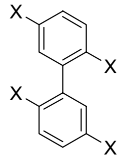
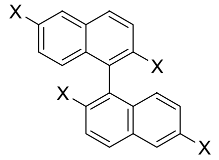
We are interested in the design of supramolecular porous chiral layers. Recently, we have investigated self-assembly of two biphenyl-2,2´,5,5´-tetrasubstituted tectons (***I***) and demonstrated formation of infinite homochiral grids set up from hydrogen-bonded cyclotetrameric compartments[1]. Now we have prepared and examined the isosteric 1,1´-binaphthalene-2,2´,6,6´-tetracarboxylic acid ***II*** distinguished by the expanded biaryl core.



I (X = COOH, CONH$_2$)



II (X = COOH)

As we have found, the racemic tecton ***II*** self-assembles again under formation of hydrogen-bonded grids set up from the expanded cyclotetrameric compartments. In contrast to tectons ***I***, empty space inside of individual cyclomeric pores now invites to interpenetration which is uniquely attained by catenation of two separate homochiral grids build up from the opposite enantiomers (Fig. 1).

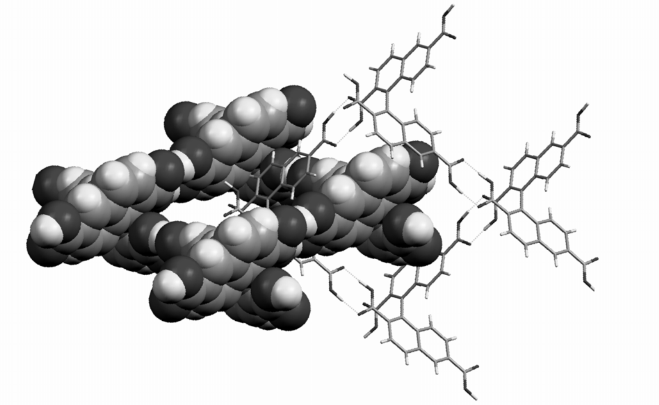


Fig. 1

The financial support of the Grant Agency of the Czech Republic (grant No. 203/03/0087) is warmly acknowledged.

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INTERACTIONS OF SELF-ASSEMBLED MONOLAYER OF METALLOPORPHYRIN-TRIS-GUANOSINE DERIVATIVE WITH NUCLEOTIDE-5´-MONOPHOSPHATES IN AQUEOUS MEDIA OBSERVED BY SURFACE ENHANCED RAMAN SCATTERING SPECTROSCOPY

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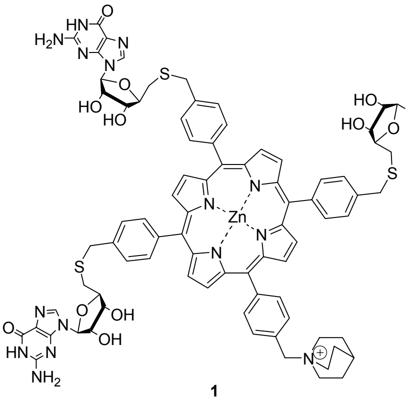

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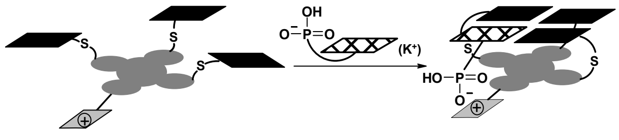
Novel porphyrin derivative with three pendant guanosine groups **1** has been prepared[1] to allow study of formation of guanosine quadruplexes in water solutions. Zn(II) metallocomplex was prepared to enable self-assembled monolayer preparation[2].

Interaction of immobilized **1** with nucleotide-5´-monophosphates in aqueous solution was studied. Our results show strong selectivity for guanidine-5´-monophosphate over other monophosphates. The results obtained here support the hypothesis of formation of guanosine quadruplex (Scheme 1).



Scheme 1. Supposed guanosine quadruplex formation.

Authors gratefully acknowledge financial support of the Ministry of Education of the Czech Republic (MSM 223400008).This work is also supporting by Hans-Fischer Foundation and Howard Hughes Medical Institute

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RECOGNITION OF CZECH BEERS BY ARRAY OF “COATED-WIRE” ELECTRODES

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Platinum electrodes coated with electropolymeric films can act as ion-selective electrodes. Their recognition properties are controlled by content of selective groups incorporated into the film.

Array of “coated-wire” electrodes based on hydroxyporphyrine film modified by metalation from organic solution was used for recognition of beer from Popovice, Pilsen and Braník Breweries. The influence of regeneration solution based on acetate buffer, borate solution and cationic surfactant solution was explored. The from in-lab developed control software were evaluated by PCA.

The system is now capable to distinguish three beers (Fig. 1), which were used as model, and not surprisingly it recognize washing solution.

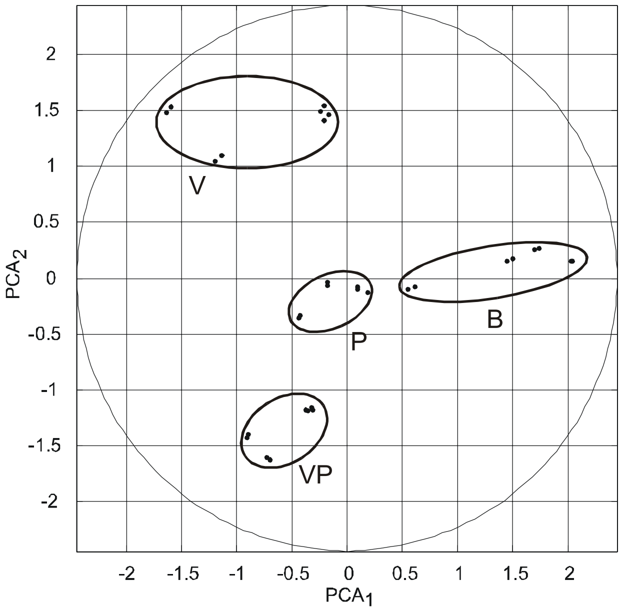

Fig. 1. The PCA plot of array response, V...regeneration solution, P...Pilsen beer, VP...Popovice beer, B...Braník beer.

This work was supported by grant of Ministry of Education, Youth and Sports of the Czech Republic (MSM 223400008)

CONSTRUCTION OF MULTICHANNEL POTENTIOMETRIC ANALYSATOR – ELECTRONIC TONGUE

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Working on a new field of chemistry often requires application of instruments, which are not commercially available. Herein we present sixteen-channel potentiometric analyzer for "electronic tongue" measurement (Fig. 1). The instrument is built into the air thermostat with precision 0.01 °C and is controlled by computer. Replaceable flow cell enables measurement of various types of electrodes (incl. PVC membrane ion-selective electrodes or "coated wire" electrodes). Inside the thermostat unit the J-FET followers are placed to avoid temperature drift. Signal from followers is measured by data acquisition card in computer. The transport of sample is operated by computer controlled (RS 232) peristaltic pump and connection of autosampler AE200 is possible.

System is controlled by software written in LabView 6.1 environment and compiled into the executable file by Application Builder for LabView. The data can be evaluated in meaning of single electrodes or as complex system by PCA or other pattern recognition method. This evaluation is not performed by LabView routines, because its insufficient numeric precision, but by Matlab script. The measurement program calls Matlab and hand data and then takes results and presents them on screen. Whole operation is transparent toward user.

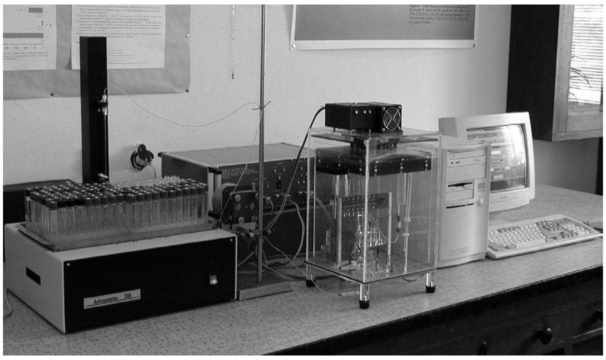

Fig. 1. The multichannel potentiometric analysator

This work was supported by grant of Ministry of Education, Youth and Sports of the Czech Republic (MSM 223400008).

SYNTHESIS OF NOVEL CHIRAL POLYAZAMACROCYCLES BY THE NON-TEMPLATED (3+3)-CYCLOCONDENSATION

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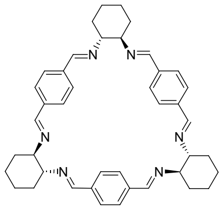
Recently, an unique reaction between enantiomerically pure *trans*-1*R*,2*R*-diaminocyclohexane and terephthaldehyde giving the product of the (3+3)-cyclocondensation in almost quantitative yield has been discovered. The chiral molecular triangles **I** are created in the absence of a template or without using a method of high dilution[1,2]. Hexaamine **II** was obtained after an easy reduction of Schiff base **I** in high yield. Complexation studies have revealed selectivity of **II** for benzene-1,3,5-tricarboxylate[3].



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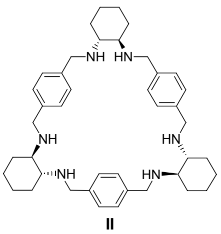

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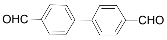
The aim of our current studies is finding of the general scope and limits of this highly efficient approach to novel chiral polyazamacrocycles. We are studying the (3+3)-cyclocondensation reaction between *trans*-1*R*,2*R*-diaminocyclohexane and other rigid aromatic dialdehydes **III-VII**, which have been prepared by a yet unpublished synthetic method utilising the Suzuki-Miyaura coupling. Our research is also focused on the extension of this unique macrocyclisation to the formation of dynamic combinatorial libraries.



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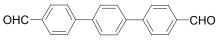

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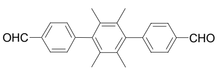

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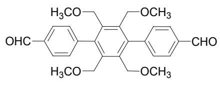

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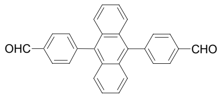

VII

The authors are indebted to AV ČR (project Z4055905) and GA ČR (203/03/0087) for financial support.

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RECOGNITION AND SELECTION OF OLIGOPEPTIDE HELICES BY SUPRAMOLECULAR APPROACH

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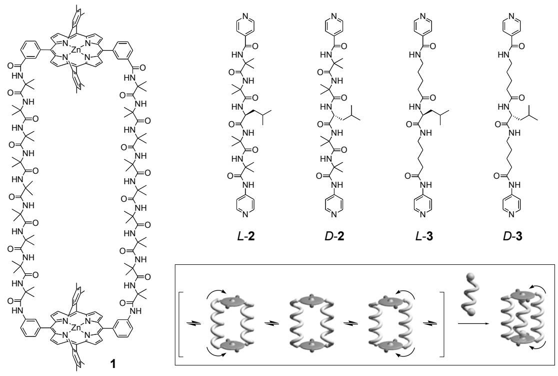

Scheme 1. Schematic structure of compound ***1-3*** and representation of chiroptical transcription of helical information.

By using biologically important "peptide bundling" as the motif, in conjunction with coordination chemistry of metalloporphyrins, we developed a novel system to sense helical conformations of oligopeptides. We synthesized a cyclodimeric zinc porphyrin host (***1***) bearing a guest–binding cavity with oligo(aminoisobutyric acid) (Aib) peptidic posts (Scheme 1). Although poly(Aib) is devoid of any chiral centers, it is known to adopt a dynamic helical structure, which switches back and forth between right- and left-handed forms. We found that ***1*** becomes optically active through stereochemical interactions with pyridine–anchored helical guests ***2*** upon inclusion in its cavity (Scheme1).

On the basis of spectroscopic titration and Job's plots, ***1*** was found to form a stable 1:1 inclusion complex in $CHCl_3$ with (*L*)-leucine–containing helical guest ***L-2*** (association constant $K_{assoc} = 1.7 \times 10^6$ M^{-1}). Although ***1*** is CD-silent, inclusion complex ***1⊃L-2*** displayed an intense exciton-coupled CD signal at the Soret absorption band of the zinc porphyrin moieties (410–450 nm), while ***1⊃D-2*** showed a mirror–image CD spectrum of ***1⊃L-2***. These observations suggest that the two zinc porphyrin units of ***1***, upon inclusion with helical ***2***, adopt a twisted geometry in either clockwise or anticlockwise manner depending on the helical sense of the guest. In sharp contrast, when a nonhelical guest such as ***L-3*** was used for the complexation with ***1***, a CD-silent inclusion complex with a much smaller association constant ($K_{assoc} = 0.04 \times 10^6$ M^{-1}) resulted. Therefore, it is most likely that inclusion of the guest with a helical conformation plays an essential role in generating a twisted geometry of the two facing zinc porphyrin units.

A NEW AND FACILE SYNTHESIS OF BILINDIONES AND BILADIONES FROM TETRAARYLPORPHYRINS

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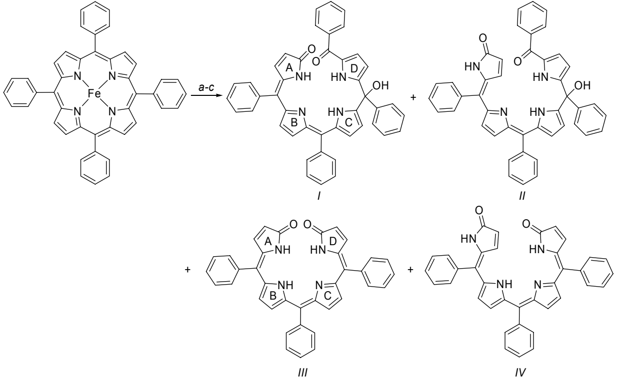
Bilindione is a pigment involved in a plant as a prosthetic group of a photo-receptor protein. Bilindione[1] has several unique features as a functional molecule such as (1) photochemical reactivity including visible-light absorption, cis-trans isomerization and photochromism, (2) excited energy transfer, (3) chiroptical properties due to the cyclic helical conformation[2], (4) redox activity, (5) coordination to various metals, and (6) reconstitution into proteins. The preparation of bilindiones required a multi-step synthesis, and a new synthetic route to bilindiones should make the compounds attractive as a scaffold of functional materials. We report here that the coupled oxidation of [tetraarylporphyrinato]iron(II) proceeds under mild conditions to yield both bilindiones and biladienones in a moderate to good yield.

Reaction of [tetraphenylporphyrinato]iron(II) with molecular oxygen, ascorbic acid, and pyridine in chloroform proceeded smoothly at room temperature to afford biladienones[3] ***I*** and ***II*** in 63 and 15 % yield, respectively.



Scheme 1. a) O_2, ascorbic acid, pyridine, b) $NaBF_4$, c) 1M HCl.

When the reaction was carried out under reflux, bilindiones ***III*** and ***IV*** were obtained in 23 and 23 % yield, respectively. The products were isolated after silica gel column chromatography. These compounds were characterized by ^1H NMR, ^{13}C NMR, COSY, NOESY, HSQC, and HMBC spectra, UV-vis and mass spectra. Bilindione ***III*** was further characterized by X-ray crystallographic analysis for the crystal obtained by slow diffusion of hexane to the chloroform solution of ***III***. The crystal structure confirmed that ***III*** is the cyclic *ZZZ*, *syn, syn, syn* isomer (Fig. 1). In the crystal, the helicoidal molecules form a homochiral column as a result of intermolecular hydrogen bonding between NH of A-pyrrole and CO of D-pyrrole (Fig. 2).

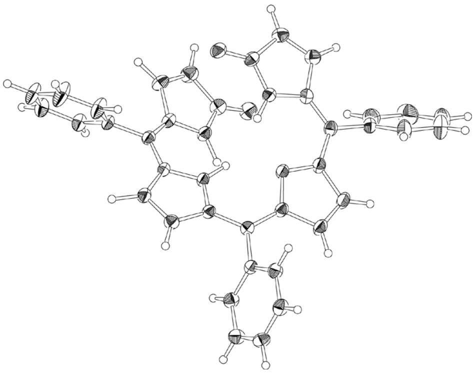


Fig. 1. ORTEP view of *III* with thermal ellipsoids at 30% probability.

Biladienone ***II*** can be photochemically isomerized to ***I***, while the reverse isomerization did not proceed. Bilindione ***III*** can be photochemically isomerized to ***IV***, and the reverse isomerization also proceeded. The photochemical stationary mixture contained ***III*** and ***IV*** in almost equimolar amounts.

The oxidation of [tetraarylporphyrinato]iron(II) also proceeded starting from 4-alkyl, 4-methoxy, 4-cyano-[tetraarylporphyrinato]iron, demonstrating the synthetic versatility of the present reaction.

In summary, a new and facile synthetic route to bilindiones was established. The study of photochemistry and coordination chemistry is currently underway.

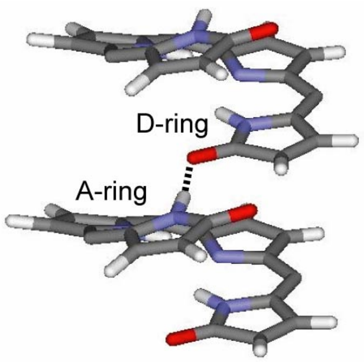


Fig. 2. Stacking of ***III*** forms a homochiral column of helicoidal molecules in the crystal. The distance between the (N)-H of the A-ring pyrrole and (C=)O of the D-ring pyrrole was 2.8 Å.

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UNSYMMETRICALLY FUNCTIONALIZED 1,1'-BINAPHTHALENES AS LIGANDS FOR THE RECOGNITION OF CHIRAL ZWITTERIONS

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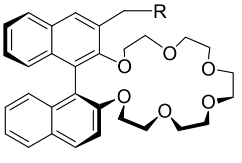
In the field of molecular recognition much interest has been focused on amino acids as important class of biomolecules[1].

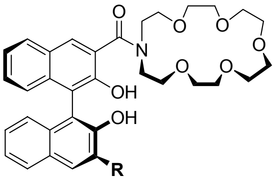
Our ligands are composed of three basic units. The central axially chiral 1,1´-binaphthalene platform, which carries two other structural parts: the binding site for ammonium cation (crown ether ring) and the binding site for carboxylate anion (urea, thiourea or amide fragment).

We utilized two different synthetic approaches: i) unsymmetrical functionalization of known optically active binaphthyl precursors[2], ii) unsymmetrical coupling of the suitably substituted 2-naphthols [3]. The first synthetic way led to the compounds ***I***, the second one was used for the preparation of ***II***.

The molecular recognition and transport properties of the synthesized ligands are investigated.



I



II

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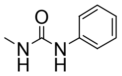

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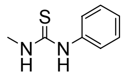

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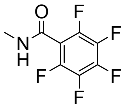

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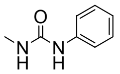

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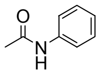

The authors are indebted to AV ČR (project Z4 055 905) and GA ČR (203/01/0067) for financial support.

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SELF-ASSEMBLED PRISMATIC ALTITUDINAL ROTORS

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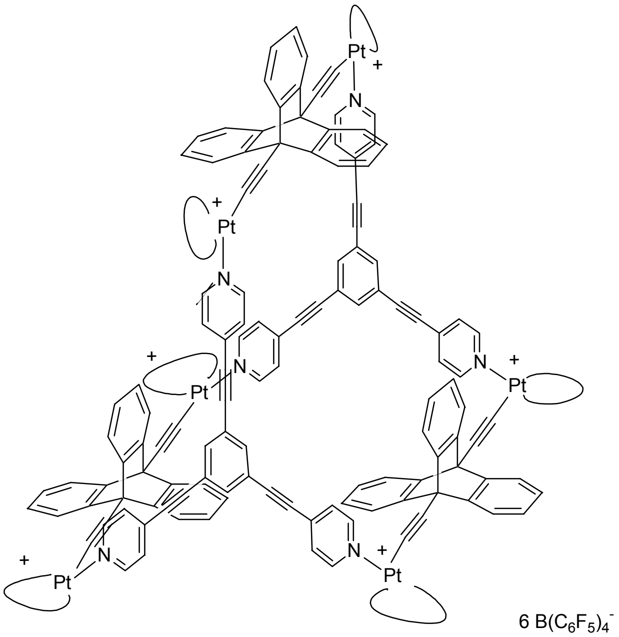
Transition metal mediated, coordination driven self-assembly[1] is used as a path towards prismatic molecular rotors. We use transversely reactive terminally metalated molecular rods and star-shaped connectors carrying a radially directed ligand at each arm end. We have examined the self assembly of digonal, trigonal, and tetragonal connectors carrying pyridine-terminated arms with molecular rods that terminate with $–Pt(+)[Ph_2P(CH_2)_3PPh_2]X(-)$ substituents[2]. The requirement of nearly free rotation for the rotator makes it difficult to fix the dihedral angle between the transverse directions dictated by the terminal coordination sites on the rod, thus rendering the organometallic rods less effective as shape defining units. We have found conditions that lead to the production of the desired structures, a rectangle, a trigonal prism, and a tetragonal prism from the respective connectors. Incorporation of a triptycene rotator into the organometallic rod yields **1**.



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SELF-ASSEMBLY AND SURFACE-MOUNTED MOLECULAR ROTORS

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One of the long-term goals of our effort in the area of molecular "Tinkertoy" construction kits is the fabrication of surfaces covered with molecular-size rotors, both of the azimuthal (rotor axle perpendicular to the surface) and of the altitudinal (rotor axle parallel to the surface) types. Molecular self-assembly enters into this effort at two levels: (i) in the synthesis of the rotors themselves and (ii) in the organization of the rotors into regular assemblies.

(i) Rotor synthesis. We shall describe briefly the preparation, characterization, and performance of an altitudinal rotor prepared by conventional covalent synthesis and mounted on a gold substrate[1]. In an effort to increase the separation of the axle from the surface and to simplify the synthesis at the same time, we have turned to self-assembly of larger rotors based on metal coordination chemistry[2]. This effort has led to the preparation of large prismatic altitudinal molecular rotors in just a few steps, and their surface mounting is presently under investigation.

(ii) Rotor arrays. Arranging surface-mounting rotors into regular arrays in which they could exhibit synergistic collective motion is of paramount importance in many potential applications. Trigonal and hexagonal arrays of dipolar azimuthal rotors are of particular significance since they offer the possibility of a ferroelectric ground state, but arrays of altitudinal rotors would be valuable as well. We shall describe the present state of our efforts to develop procedures for the self-assembly of two-dimensionally crystalline grids on surfaces of liquids and their transfer to surfaces of solids[3].

This project has been supported by the USARO, grant DAAD19-01-1-0521

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CYCLOIPTYCENES: ELUSIVE TECTONES FOR SELF-ASSEMBLY OF RIGID POROUS FRAMEWORKS

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Design of porous architectures attracts much attention inspired by a broad variety of potential applications in molecular recognition, catalysis, gas storage and separation[1]. Supramolecular stacking of rigid macrocyclic compounds represents one of the most promising approaches, designed self-assemblies of tailor-made cyclopeptide and cyclosaccharide tectones being prominent examples[2].

Conceptually, cycloiptycenes (*e.g*. Fig. 1) may be viewed as interesting alternative tectones offering a wide-bore rigid cylindric interior (d = cca 10Å) together with optimal orientation of the prospective substituents (X) for the generation of requisite supramolecular links.

Up to now, attempts at synthesis of the challenging cycloiptycene structure failed[3]. Our novel access en route to the elusive target based on the repetitive [4+2] cycloaddition reaction will be described.

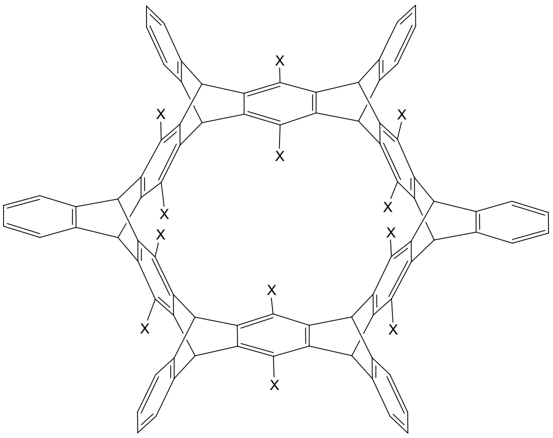

Fig. 1

Financial support from the Grant Agency of the Czech Republic (grant No. 203/03/0087) is gratefully acknowledged.

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SYNTHESIS AND SELF-ASSEMBLY OF TRIPTYCENE CARBOXYLIC ACIDS

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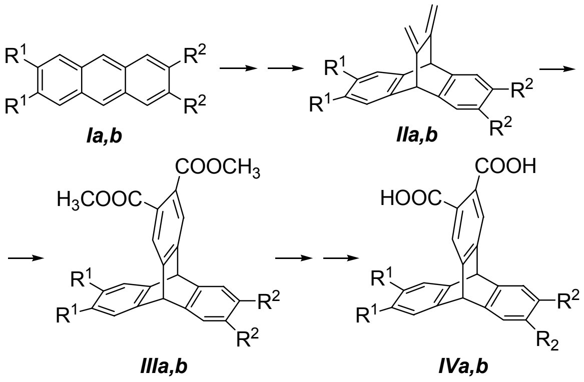
The triptycene molecules with various number of carboxylic functions represent interesting building blocks for molecular self-assembly. It is supposed that such rigid carboxylic tectons could self-assemble into hollow channels organized by intermolecular hydrogen bonds.

Starting compounds are methyl-substituted antracenes ***I*** which are prepared according to known procedures[1,2]. Addition of 1,4-dichlorobut-2-ene[3] on the antracenes ***I*** followed by dehydrohalogenation yields dienes ***II***. The exo-dienes ***II*** react with dimethyl acetylenedicarboxylate[4] and thus obtained adducts undergo aromatization (DDQ) forming triptycene derivatives ***III***. Finally, hydrolysis of the ester groups and oxidation of the methyl-substituents leads to the target triptycene acids ***IV***.



Ia-IIIa $R^1 = R^2 = CH_3$
Ib-IIIb $R^1 = H$, $R^2 = CH_3$
IVa $R^1 = R^2 = COOH$
IVb $R^1 = H$, $R^2 = COOH$

The self-assembly of the prepared compounds in the crystalline phase is being studied by X-ray analysis.

The authors are grateful for the financial support from the Grant Agency of the Czech Republic (grant No. 203/03/0087).

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SIMPLE MYOGLOBIN MODEL COMPOSED OF PERMETHYLATED β-CYCLODEXTRIN DIMER AND WATER-SOLUBLE Fe(II)PORPHYRIN

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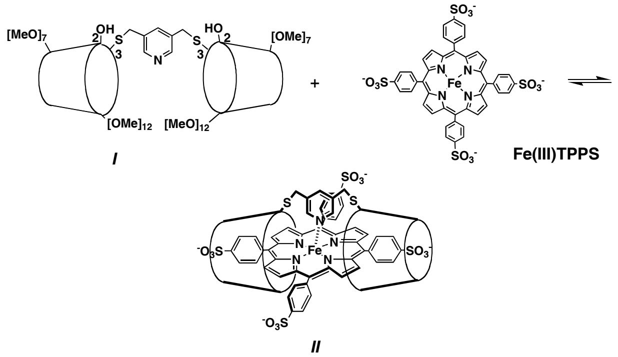
In 1974, Collman and co-workers reported a first example of myoglobin (Mb) model using a picket-fence porphyrin[1]. After that, various Mb models have been designed and prepared to protect formation of μ-oxo dimers and six coordinate Fe(II)porphyrins[2]. Most of these studies were carried out in organic solvents and very few examples have been reported with O_2 binding to Mb models in protic solvents. Recently, Zhou and Groves synthesized a hemoprotein model involving a cyclodextrin substructure that works in aqueous solution[3]. Their model compound, however, is so complex that there is a problem of versatility. In the present study, we found that a per-*O*-methylated β-cyclodextrin dimer containing a pyridine bridge (***I***) forms an inclusion complex of Fe(III)TPPS (TPPS = *meso*-tetrakis(*p*-sulfonatophenyl)porphyrin) (***II***) whose Fe(II) form binds O_2 reversibly in aqueous solution.

Compound ***I*** incorporated Fe(III)TPPS into its cavities to form ***II*** that was extremely stable in aqueous solution. UV-vis absorption spectral changes of Fe(III)TPPS was halted upon addition of an equimolar amount of ***I***, indicating the formation of a stable 1:1 complex. ^{1}H NMR spectrum of ***II*** in D_2O showed the signals due to the pyrrole β-protons at 51, 53, and 55 ppm (standard: TSP) at pD 4.4. These chemical shifts indicate the generation of a five coordinate admixed spin state. At pD 8.7, the pyrrole β-protons showed the broad signals at ca. 84 ppm, suggesting the formation of a high spin mono-hydroxo Fe(III) complex.



Complex ***II*** in aqueous solution at pH 4.5 was reduced by $Na_2S_2O_4$ under Ar atmosphere. The reduction product had a Soret band at 434 nm, which was ascribed to Fe(II)TPPS. Introducing O_2 into the solution of the Fe(II) form of ***II*** caused the blue shift of the Soret band (423 nm), which shifted again to 422 nm by replacing the atmosphere of O_2 with CO (Fig. 1).

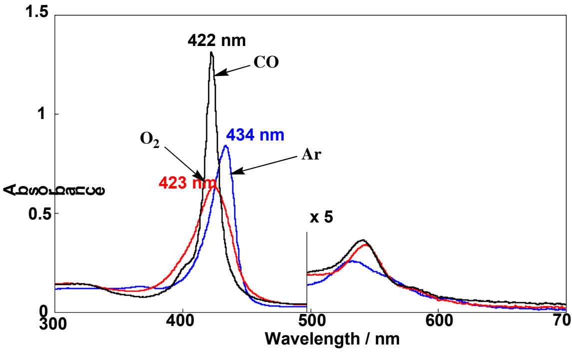


Fig. 1. Absorption spectra of five coordinate Fe(II) complex of ***II*** formed by the action of $Na_2S_2O_4$, O_2 adduct of Fe(II) form of ***II***, and CO adduct formed by reaction of the Fe(II)(O_2) complex with CO in aqueous solution at pH 4.5.

These absorption spectral data strongly suggest that the O_2 molecule is bound to the five coordinate Fe(II) complex of ***II*** to yield a six coordinate O_2 adduct, from which the O_2 molecule was removed by introducing a stronger ligand CO into the system. The formation of the six coordinate Fe(II)(O_2) complex was supported by ^{1}H NMR spectrum. Namely, the pyrrole β-protons of the O_2 adduct appeared at ca. 8-9 ppm. Such upfield shifts suggest the formation of a six coordinate low spin state. In addition, a Fe-O stretching band was observed at 569 cm^{-1} that shifted to 546 cm^{-1} by replacing $^{16}O_2$ with $^{18}O_2$ in the resonance Raman spectrum of the O_2 adduct of reduced ***II***.

The half-lifetimes ($t_{1/2}$) of the O_2 adduct of the Fe(II) complex of II under air were measured by means of absorption spectroscopy. At pH 4.5 (succinic acid buffer), $t_{1/2}$ was 12.0 h, while it was elongated to 16.9 h at pH 6.0 (succinic acid buffer). Although reason has not been clarified yet, $t_{1/2}$ became longer when the phosphate buffer was used. Presumably, a CO_2^- group of succinate ion is weakly bound to Fe(II) to cause the release of O_2.

The dioxygen was removed from the Fe(II)(O_2) complex when the atmosphere of the system was replaced by Ar, indicating the occurrence of reversible O_2 uptake. The O_2 uptake-release cycles were possible to repeat several times.

The present results show that the compound ***II*** and its Fe(II) complex are excellent metMb and Mb functional models, respectively.

The authors acknowledge Professor T. Kitagawa at Institute of Molecular Science and Technology for his wonderful discussion on resonance Raman spectroscopy.

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COMPLEXING BEHAVIOR OF POLYPEPTIDE-SHELLED DENDRIMERS

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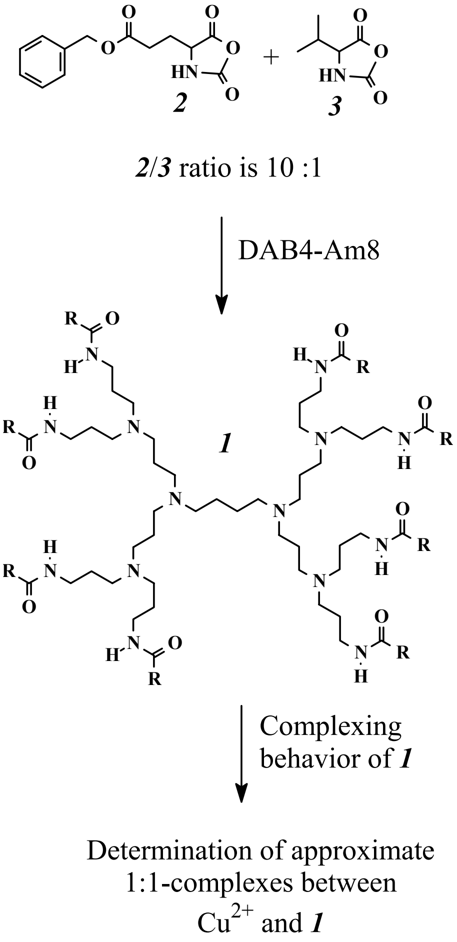
The ring-opening polymerization of α-amino acid *N*-carboxyanhydrides (NCAs) offers a well-established working tool to realize different polypeptide derivatives[1].



Scheme 1. Polypeptide-shelled dendrimer ***1*** with DAB4-Am8 core – R = poly(γ-benzyl-L-glutamate-co-DL-valine) arms

Thus, investigations of the polypeptide conformation and their applications to various fields were reported in the last decade. Also, star-shaped polypeptides[2] were successfully synthesized by applying NCA ring-opening polymerization. The outcome of this structural feature was the enhancement of the tertiary structure, especially in aqueous solution, which let act such polypeptides as artificial proteins or container molecules. The last approach culminated in the preparation of polypeptide-shelled dendrimers[3]. These molecules showed enantioselective binding and stable encapsulation of α-amino acids in aqueous solution. Polypeptides with defined three-dimensional structure are important for the development and improvement of functions (*e.g.* controlled release) based on polypeptide materials.

The concept of polypeptide-shelled dendrimers was applied to study the complexation properties of polypeptide-shelled dendrimers with Cu^{2+} ions. The background for these investigations is the lack of enhanced stability of low-molecular-weight radionuclide complexes in cancer therapy due to the absence of protection shells in such complexes towards biological systems. Three-dimensional protection shells, caused by additionally attached polypeptides to dendrimer surfaces, are the fundamental prerequisite to enhance the biological functionality of dendritic metal complexes.

Different polypeptide-shelled poly(propylene imine) dendrimers ***1*** (Scheme 1) were prepared by NCA polymerization of compound ***2*** and ***3*** with the dendrimer DAB4-Am8 as initiator and core. Different molecular weights up to 20 x 10^3 g/mol were determined by SEC. NMR analysis and MALDI-TOF-MS investigations supported the presence of (co-)polypeptide structures on the dendrimer surfaces. These polypeptides were used as model compounds for the study of complexation between non-radionuclides and surface-modified dendrimers, firstly. Microcalorimetric titration measurements in DMSO as solvent revealed the formation of strong complexes between Cu^{2+} ions and polypeptide-shelled dendrimers ***1*** with an approximate ion to ligand ***1*** ratio of 1:1. In contrast, the results of unmodified dendrimer DAB4-Am8 indicate a higher stoichiometric ratio of Cu^{2+} ion binding (appr. 4:1) to the dendrimer. It can be concluded that wrapping polypeptide chains on dendrimer surfaces can reduce the number of Cu^{2+} ions complexed by the dendrimer interior.

The authors gratefully thank the Saxony Ministry of Science and Art (Project-No 7531-50-03-0370-01/4) for financial support. The authors thank Mrs. U. Stephan for carrying out the NCA polymerisation experiments. The authors thank Dr. D. Kuckling (Dresden University of Technology) for carrying out MALDI-TOF-MS investigations.

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FUNCTIONAL LAYERS BASED ON QUATERNIZED ALKALOID BRUCINE – PREPARATION OF THIN POLYMERIC FILMS, THEIR CHARACTERIZATION AND USING FOR ANION RECOGNITION

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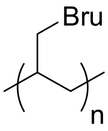
Rigid chiral scaffold of alkaloid brucine with a number of functional groups represents very potential unit for molecular recognition. To provide study of interaction on the interface, we use *N*-alkylation of brucine to allow its covalent immobilization. We showed the vitality of this concept on brucine quaternized by 6-bromohexanoic acid and on further using of the product for enantioseparation of some organic carboxylates[1].

Here we present the preparation of thin polymeric films derived from brucine quaternized by allyl bromide (***1***) and 6-bromohex-1-ene (***2***). Further polymeric films were derived from 2-aminophenol (***3***) and 3-aminophenol (***4***). In these cases brucine units were attached *via* trisbrommethylmesitylen. Cyclic voltametry was used for monitoring of film grow and Surface Enhanced Raman Scattering (SERS) spectroscopy was used for final characterization. Prepared polymeric films were tested for interactions with model anionic species by potentiometry.



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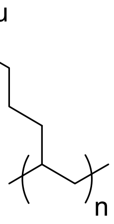

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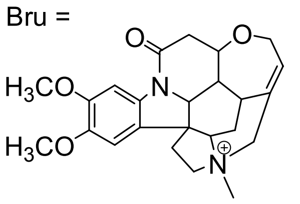

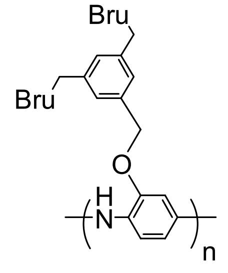

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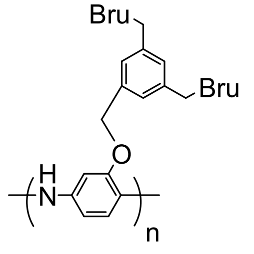

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ELECTROPOLYMERIZATION OF 8-AMINOQUINOLINE AND CHARACTERIZATION OF THE SYNTHESIZED POLYMERIC FILM

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Electrochemical polymerization is widely used for preparation of corrosion protective coatings, organic electronic devices, chemical- and biological sensors and other devices and functional coatings[1]. Such substances as phenol, 1-aminoanthracene can be polymerized directly. We describe here electrochemical polymerization of 8-aminoquinoline. This compound is suggestive to be polymerized through amino group or/and nitrogen in the pyridine ring.

The polymerization was performed in sulphuric acid by cyclic voltammetry. No increase of current, which is typical for formation of highly conductive polymers, was observed. An electrochemical deposition of poly(8-aminoquinoline) on thin films of polyaniline led to the shift of oxidation / reduction peaks of polyaniline followed by a suppressing of the electrochemical activity of polyaniline.

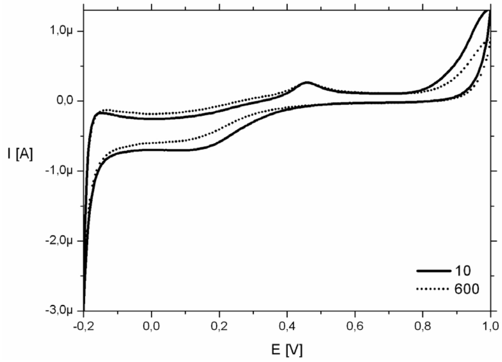

Fig. 1. Cyclic voltammogram of polymerization of 8-aminoquinoline

The polymer films were characterized by optical microscopy and investigated electrochemically. The films are optically homogenious and display a non-intensive dark colour. Electrochemical characterization was performed by cyclic voltammetry and electrochemical impedance spectroscopy. The voltammograms indicate on three oxidation states of the polymer. An increasing of pH results in a decreasing of the electrochemical activity. Impedance spectra are pH- and potential dependent. Comparison of the impedance spectra of polyaniline and poly(8-aminoquinoline) with polyaniline sublayer confirmed the increase of total film resistance.

Financial support from Ministry of Education, Youth and Sports of the Czech Republic (MSM 223400008) is gratefully acknowledged.

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COMPLEXATION OF METAL IONS BY POLYANIONIC AND ZWITTERIONIC OLIGOPYRROLIC MACROCYCLES

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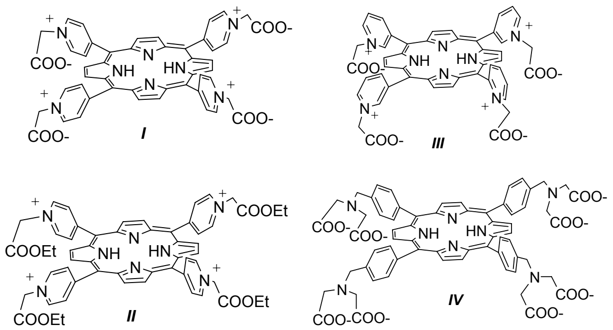
Porphyrins are oligopyrrolic macrocycles, which play a vital role in living organisms. They are parts of many enzymes, vitamins, crucial role of porphyrins in haemoglobin or chlorophyl are generally known[1].

In all this compounds, porphyrins are present as metal complexes. Synthetic metal complexes of porphyrin are used as photosensitisers for photodynamic therapy (PDT) of tumors[2], interact with DNA[3] and for their catalytic properties are used as catalyst in many reactions[4].

For their optical properties, porphyrins are very important for spectroscopic study of their complexation ability. We prepared some compound, that contain porphyrin core as good chromophore unit and many carboxylate group on porphyrine periphery as chelatation unit for metals.

Our goal is to develope receptors for biologycally important compounds as nucleic acids, aminoacids, aminosaccharides and other saccharide derivates and porphyrin chelates of metals can one way to purpose. The observed results of metal binding by receptors ***I-IV*** will be presented.



Scheme 1. Receptors ***I*** - ***IV***

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POLY(AMINOBENZOTHIADIAZOLE) AS A NEW MATERIAL. ELECTROCHEMICAL SYNTHESIS AND CHARACTERIZATION

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The progress in the material science during the last decade and establishing of new application fields demonstrated an importance of searching for new materials, especially that ones which can be polymerized directly on conductive surfaces. We present here a new polymer - poly(4-aminobenzo-2,1,3-thiadiazole).

The chemical synthesis of the monomer-precursor and its chemical and physical properties are described in [1,2]. We found conditions for electrochemical polymerization of this compound on Pt surface. This reaction was performed by cycling of the electrode potential in aqueous medium (3 M sulfuric acid (Fig.1) or 0.1 M phosphate buffer with pH 3.0) or in organic medium (0.05 M Bu_4NClO_4 in acetonitrile). The electropolymerization leads to the formation of visible color films. Optical microscopy demonstrated their grains-formed structure. At neutral pH the polymer films formed in aqueous electrolytes displayed electrochemical activity and at least three oxidative states while no electrochemical activity observed at acidic or alkalic pH. Electrochemical impedance spectroscopy demonstrated strong influence of pH, electrode potential and preparation conditions.

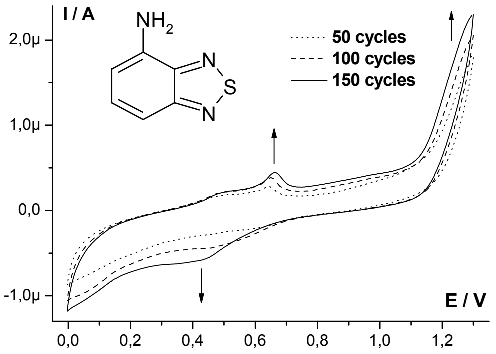

Fig. 1: Polymerization of aminobenzothiadiazole in sulphuric acid

Financial support from Ministry of Education, Youth and Sports of the Czech Republic (MSM 223400008) is gratefully acknowledged.

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TWO NOVEL PORPHYRIN-β-CYCLODEXTRIN CONJUGATES AS POSSIBLE AGENTS OF PDT: BIOLOCALISATION AND INTERACTION WITH SERUM DRUG CARRIERS

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Two water-soluble fluorinated *meso*-tetraphenylporphyrin conjugates with one (***I***) or two (***II***) molecules of β-cyclodextrin were prepared and analysed as possible agents for photodynamic therapy (PDT) of cancer. The aim of this study is to compare *in vivo* and *in vitro* biolocalisation properties of these compounds as well as their interactions with serum drug carriers, i.e. human serum albumin (HSA), high and low density lipoproteins (HDL and LDL). The *in vivo* experiments were performed on BALB/c mice bearing subcutaneously transplanted syngeneic mouse mammary carcinoma, 4T1, and *in vitro* study on cell line 4T1. Drug localisation in tissues and cells was detected by fluorescent spectroscopy. The interaction of photosensitisers with HSA, HDL and LDL was studied by fluorescence spectroscopic titration. The results of *in vivo* biodistribution experiments show first that both compounds accumulate in tumor tissues at higher extend than in normal tissues suggesting tumour specificity. Second, compound ***II is*** rapidly releaseed from tissues, whereas compound ***I*** shows significantly slower clearance. The *in vitro* study demonstrates that both photosensitisers localised mainly in lysosomes and compound ***I*** exhibits significantly higher cell uptake than compound ***II***. Based on fluorescence titration experiments, HDL and HSA seem to be the main serum carriers for compounds ***I*** and ***II***, respectively. The observed differences between mono- and bis-cyclodextrin-porphyrin sensitizers likely results from more polar character of compound ***II***.

Financial support from Czech grant agency (grant No. 309/02/1193, 301/04/1315, and 203/02/0420), grant of the Ministry of Education, Youth and Sports of the Czech Republic (MSM223400008) are gratefully acknowledged.

INTERACTION OF TWO SAPPHYRIN-POLYAMIN CONJUGATES WITH MODEL ANIONIC BIOPOLYMERS

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The interactions of two sapphyrin-polyamin conjugates, which contain two (***I***) or four (***II***) aminogroups per one macrocycle, with various model biopolymers were studied by UV-vis spectroscopic titration and by electronic CD. Bovine serum albumin (BSA), poly(Glu), and anionic polysaccharides (carboxylated - alginate, pectate, pectinates of various DM values and hyaluronate; sulphated - carrageenans and heparin) were chosen as model compounds. Titration of ***I*** and ***II*** with studied biopolymers was followed by Soret band blue shift with significant hypochromism, i.e. from 420 nm to 398-400 nm. CD spectra showed an intense negative band corresponded to this blue shifted absorption band. This spectral feature indicates the formation of highly ordered aggregated macrocycles arranged on the backbone of these biopolymers. Two red shifted bands of sapphyrins at 424 and 456 nm appeared at higher concentration of polysaccharides. These bands assigned to dimeric and monomeric macrocycles, respectively, indicate subsequent de-aggregation of sapphyrins. In comparison with pectate, methyl ester groups in pectinates markedly inhibited dissociation of sapphyrin aggregates. Observed results of UV-vis spectroscopic titration for sapphyrins-polyamin conjugates confirm the importance of ionic interaction in stabilisation of non-covalent complexes between sapphyrins and anionic biopolymers in aqueous solutions.

Financial support from Czech grant agency (grant No. 301/98/K042, 309/02/1193, 301/04/1315, and 203/02/0420), grant of the Ministry of Education, Youth and Sports of the Czech Republic (MSM223400008) are gratefully acknowledged.

INTERACTION OF ANIONIC PORPHYRINS WITH CHITOSAN

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Organised chromophore assemblies are interesting for such research areas as light harvesting, molecular electronics and chemotherapy. Such organised structures have involved covalent links between chromophores or been stabilised by weak interactions. Porphyrins and other closely related macrocycles, which may contain peripheral substituents or incorporated metal cations, have been used in many investigations as suitable chromophores. Water-soluble porphyrins are able to form supramolecular aggregates onto the surface of oppositely charged biopolymers. Therefore, electrostatic interaction between macromolecular components could promote self-forming ordered arrays.

In this work we used polysaccharide chitosan, a polymer of partially *N*-acetylated β(1,4)-linked 2-glucosamine, as a scaffold to bind porphyrins carrying anionic substituents. The interactions between chitosan and these porphyrins in aqueous solutions were analysed by electronic spectroscopy (absorption, fluorescence and ECD). Obtained results confirm the formation of highly ordered aggregates of porphyrins in the presence of chitosan. In appropriate conditions adding of anionic porphyrins to an aqueous solution of chitosan led to the rapid formation of coloured fibrous precipitate that was isolated and analysed by resonance Raman (RR) spectroscopy. According to the RR spectra, the fibrils consist of highly aggregated macrocycles bound to chitosan macromolecules. Possible structure of these porphyrin assemblies was discussed.

Financial support from Czech grant agency (grant No. 301/98/K042, 309/02/1193, 301/04/1315, and 203/02/0420), grant of the Ministry of Education, Youth and Sports of the Czech Republic (MSM223400008) and internal grant of ICT Prague No. 321080015 are gratefully acknowledged.

COMPUTATIONAL STUDY OF THE N-H DISSOCIATION IN *N,N′*-ETHYLENEBIS(4-AMINOPENT-3-EN-2-ONE) AND OF ITS INTERACTION WITH METAL ATOMS

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Condensation products of acetylacetone and related β-diketones with amines and diamines have induced a strong research due to their increased ability to coordinate metal ions. These metal complexes with uncyclic tetradentate N_2O_2-ligands are applied, among others, as second order non-linear optical materials, spin-crossovers, catalysts of asymmetric oxidations, flame retardants and photostabilizers. Thus, these important applications are accompanied with investigation of their molecular and electronic structures as well as with their reactivity. Thermodynamic parameters such as, metal-ligand bond energies, enthalpies of formation, etc., for this kind of compounds are still unknown.

The present communication is devoted to the study of the thermodynamic properties of transition metal complexes with *N,N'*-ethylenebis(4-aminopent-3-en-2-one), H_2ACACEN. One important property that is calculated is the N-H bond dissociation enthalpy, BDE, in the ligand since this parameter is required to obtain the strength of the metal-ligand bonds, *c.f.* reaction (1).

$$\mathrm{M + H_2ACACEN \rightarrow MACACEN + 2\,H} \qquad (1)$$

Reaction (1) is also used to estimate the enthalpy of formation in the gas-phase of the metal complex based on the calculated enthalpy of reaction (1) and the experimental enthalpies of formation of all species except MACACEN. The enthalpy of reaction (1) and the N-H BDEs were computed by accurate density functional theory calculations at the B3LYP/6-311+G(2d,2p)//B3LYP/6-31G(d) level of theory. This approach was successfully used in recent studies[1,2]. It consists of enthalpies computed from the energies coming from full-optimization at the B3LYP/6-311+G(2d,2p) level and incorporating corrections for T = 298.15 K computed by the B3LYP/6-31G(d) approach.

The authors are grateful to Fundação para a Ciência e a Tecnologia, FCT, Lisbon, for financial support. JRBG thanks also FCT, for his post-doctoral (SFRH/BPD/11582/2002) research grant.

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NOVEL PYRROLE BASED AND IMIDAZOLE BASED EFFICIENT AND SELECTIVE ANION RECEPTORS

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Pyrrole and imidazole derivatives are abundant ligands for different metal ions, such as Zn, Fe, Co, Hg and Cu, in many biological systems[1-3]. In contrast, both pyrrole and imidazole derivatives are also able to form strong hydrogen bonds through their “N-H” groups, which act as proton donors. Imidazole also participates in hydrogen bonding through its “N:” side, which acts as a proton acceptor.

In the last decade, different groups demonstrated the ability to use pyrrole-based receptors in order to effectively and selectively bind anionic species[4], while the role of imidazole in binding anionic species through it’s NH group is practically unexplored.

Here we report on the preparation, crystal structure and anion binding properties of different new imidazole-based and pyrrole-based effective and selective anion receptors, such as and **2**. Imidazole- based anion receptor systems are found to form strong complexes with the fluoride anion, even in aqueous DMSO. The molecular structure of the receptors reveal that destructive intramolecular hydrogen bonding is prevented by the relative geometry of the imidazole ligands.

The imidazole rings bind anionic species both through hydrogen bonds and, when protonated, through electrostatic interactions.

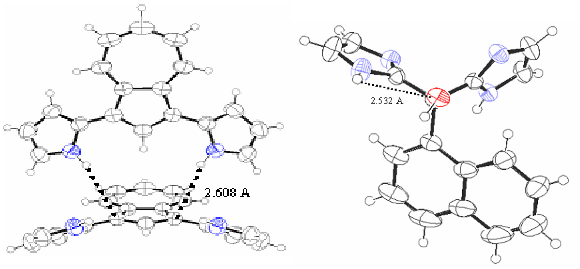

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Fig. **1.** Crystal structure of 1,3-di(2-pyrrole)azulene, **1** and bis-(1*H*-imidazole-2-yl)-naphthalene-1-yl-methanol, **2**

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MOLECULAR RECOGNITION AND STRUCTURAL CHEMISTRY OF SOME NEW ANION RECEPTORS

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Our interest in anion complexation has led us to study the anion binding properties of a variety of acyclic diamidopyrroles and diamidodipyrromethanes[1]. We found that these molecules function as oxo-anion selective hosts in solution and the solid-state. Bis-amido-dipyrromethanes have been shown to function as anion receptors in highly competitive solvent media[2].

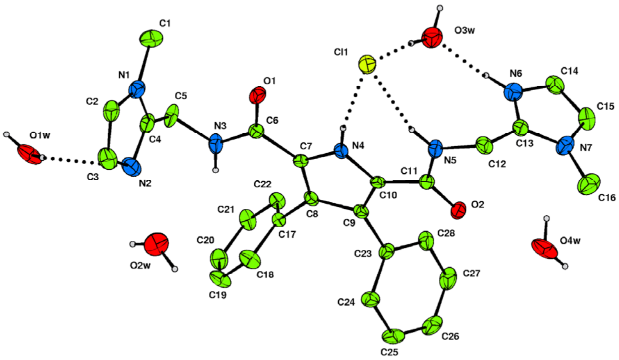

Fig. **1.** Crystal structure of the HCl complex of an imidazole functionalised bis-amidopyrrole

In collaboration with Bradley Smith's group at the University of Notre Dame, we have employed our amidopyrrole systems in receptors designed to symport HCl across lipid bilayers. These receptors have the potential of triggering apoptosis in cancer agents by transporting HCl from within endosomes inside cells into the cell endoplasm. The new receptors have been shown to symport HCl across synthetic POPC/cholesterol bilayers[3]. The crystal structure of the HCl complex of an imidazole functionalised amidopyrrole is shown below. These and other cyclic and acyclic anion receptor systems will be discussed in this lecture.

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COLORIMETRIC SENSORS BASED ON DISPLACEMENT REACTIONS IN ANION RECOGNITION

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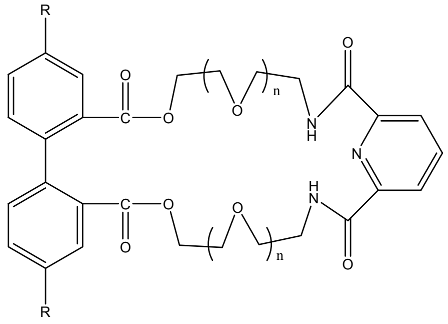
Much work has been directed to the design and synthesis of anion receptors in molecular recognition chemistry[1]. This is due to the crucial roles anions play in biology, medicine, and environment. Many chemical sensors following the approach of the covalent attachment of signalling subunits and binding sites have been reported. In these sensor molecules the change in a physical property of the host after co-ordination with the guest transmits to the macroscopic world the complexation event. Another approach to anion detection is the displacement assay. As in the above case, the signalling process is based on the use of binding sites and certain signalling subunits. However, in this approach the subunits are not covalently attached but instead form a molecular ensemble whose spectroscopic characteristics (colour or fluorescence behaviour) have to be as different as possible to those of the free signalling subunit. Then, when a target molecule is added to the solution containing the ensemble, displacement of the signalling unit takes place by the anion and the properties of the released signalling unit return to their non-coordinated state[2]. Among the signalling subunits used in this type of experiments the *p*-nitrophenolate anion has given rise to interesting results[3]. Complexation of *p*-nitrophenolate anion modifies its electronic properties giving rise to a colour change that can be used for colorimetric displacement sensing.

During the last years we have been working in the synthesis of ligands (Chart 1) derived from biphenyl and able to act as fluorescent or colorimetric sensors for cations and anions[4]. Now, we report the use of these ligands as colorimetric sensors through displacement reactions.



1 R=NO_2, n=0
2 R=$N(CH_3)_2$, n=0
3 R=NO_2, n=1
4 R=$N(CH_3)_2$, n=1

Chart 1

Ligands **1-3** were able to complex *p*-nitrophenolate as its tetrabutylammonium salt. Complexation studies were carried out using UV-vis spectroscopic techniques and with the three ligands the characteristic colour of tetrabutylammonium *p*-nitrophenolate disappears after addition of an excess of ligand. By contrast ligand **4** does not show any modification. UV-vis tritrations with the studied ligands demonstrated that the stoichiometry was 1:1. The complexation constants were determined by using the Clinp software and are shown in Table 1.

Table 1. Complexation constants of tetrabutylammonium *p*-nitrophenolate in CH_3CN at 25ºC using UV-vis spectroscopy.

Ligand	*1*	*2*	*3*
Log K	4.55±0.03	3.22±0.02	4.09±0.02

The results shown in Table 1 indicate that compounds with nitro groups in the biphenyl moiety form stronger complex than ligands containing dimethylamino groups. Thus, the complex formed by ligand **1** is ten times more stable than the complex formed by ligand **2**. These two ligands have the same both size and donor atoms being the only difference the substitution in the biphenyl system. The same behaviour is observed with ligands **3** and **4**. With these two hosts the influence of the biphenyl substitution is so strong that ligand **4** is unable to form stable complexes.

The ability of ligands **1-3** in anion complexation had been previously studied and the observed results suggested the possibility of carrying out displacement assays in order to study the behaviour of these hosts as colorimetric sensors. Thus, addition of anions to solutions of p-nitrophenolate complexes gives rise to a displacement reaction that restores the yellow colour of the free p-nitrophenolate. Fig. 1 shows the relative absorbance values for solutions of **1-3** ($3.6x10^{-5}$ M) and *p*-nitrophenolate ($3.6x10^{-5}$ M) in MeCN upon addition of different anions (until 100 equivalents).

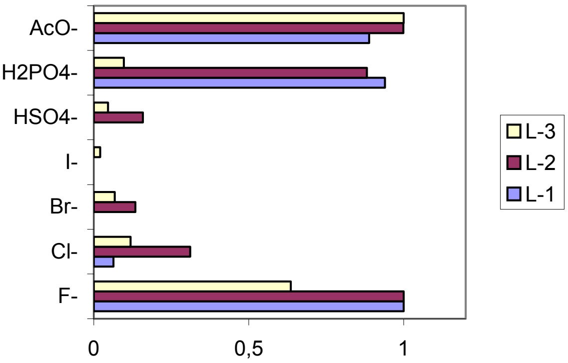


Fig. 1. Relative absorbances for solutions of **1-3** and *p*-nitrophenolate in MeCN upon addition of different anions

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SPECTROPHOTOMETRIC STUDY OF THE INTERACTION BETWEEN TCNQ AND CRYPTAND 222 IN CHLOROFORM SOLUTION

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Hundreds of different molecular complexes containing TCNQ as the acceptor have been made and studied. Some of the complexes exhibit the highest conductivity observed for organic compounds. Although the molecular complexes of TCNQ with different donors have been investigated quite extensively, few reports on the complexes of crown ethers and TCNQ have appeared. So, more study in this field is needed. We recently discussed the behavior of the molecular complexes of different crown ethers and cryptands. In this paper we report the results of spectroscopic study of complexation of TCNQ with C222 in chloroform solution.

The interaction between 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane (C222) and π - acceptor, 7,7,8,8-teracyanoquinodimethane (TCNQ) has been studied in chloroform at 25 °C. The results indicate a two step mechanism. At the first, two adducts (assigned as P1 and P2) are formed through equilibrium reactions. In continue and through nonequilibrium reactions the adducts are converted to a final product (assigned as P3). Based on the comparision of the spectra of C222-TCNQ mixture with that of Na-18C6 – TCNQ mixture the C222 $^{+}$ TCNQ^{-} , C222^{+} TCNQ^{-} TCNQ^{0} and $(C222^{+})_2$ $(TCNQ^{-})_2$ are suggested as the P1,P2, and P3, respectively. IR specra of C222 and TCNQ are compared with the spectrum of solid 1:1 TCNQ – C222 complex and the effect of complextion on absorption bands are discussed [1-4].

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SPECTROPHOTOMETIC AND ELECTROCHEMICAL STUDY OF THE INTERACTION OF CRYPTAND 222 WITH DDQ AND I_2 ETHANOL SOLUTION

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DDQ is a famous π-acceptor and its charge transfer complexs have been the subject of an extensive study. On the other hand, the complexation of iodine with a wide variety of ligands have been studied frequently. However it seems that in both cases much less attention have been paid to the complexation whit crown ethers. In addition most studies were performed in inert solvents. Thus more study with crown ethers and in noninert solvents in needed. We have been currently involved in the study of molecular complexes of crown ethers. In this paper we report the results of interaction of cryptand 222 with I_2 and DDQ in ethanol solution.

A spectrophotometric and electrochemical study concering the interaction of cyptand 222 with DDQ and I_2 has been performed in ethanol solution in the case of DDQ, the results are indicative of the formation of C222^{+} andDDQ^{-} through an equilbrium reaction in the case of I_2 the results indicate the fomation of C222^{+} & I_3^{-} through nonequilibrium reaction. The formation constant of the DDQ complex has been calculated from the absorbance- mole ratio data. using the nonlinear least square program "KINFIT". The biamperometric results proves that DDQ/DDQ^{-} behaves as and irreversible couple, however I^{-}/I_2 act as a reversible couple. The spectrophotometric and electrochemical results show that in ethanol solution a fraction of iodine converts to I_3^{-}.

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SOLVENT RELAXATION IN BIOMEMBRANES

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Solvent relaxation (SR) refers to the dynamic process of solvent reorganisation in response to an abrupt change in charge distribution of a dye via electronic excitation. While in pure water the solvent relaxation time occurs on the sub-picosecond time-scale[1], it has been shown that a significant part of solvent relaxation in phospholipid bilayers occurs on the nanosecond (ns) time scale[2]. Within the last ten years SR studies in bilayers became of interest for two different motivations: Firstly, our group demonstrated the benefit of this technique in detecting physiological relevant changes in the phospholipid bilayer organization (see *e.g.*[3,4]). Subsequently, contributions addressing the question on the origin of slow relaxation components probed in lipid membranes were published (see *e.g.*[5]).

A major requirement for valid application or physical interpretation of SR studies in bilayers is the knowledge about the location of the used chromophore. It has been demonstrated[2] that the solvent relaxation kinetics characterised by τ_r is strongly dependent on the location of the chromophore within the bilayer. The SR kinetics of dyes like 6,8-difluoro-4-heptadecyl-7-hydroxycoumarin which are probing the external interface of the bilayer occurs on a rather short time scale. About 50 % of the relaxation probed by 6,8-difluoro-4-heptadecyl-7-hydroxycoumarin in phosphatidylcholine (PC) small unilamellar vesicles at room temperature is faster than 50 ps. The second part of the solvent relaxation, on the other hand, occurs on the nanosecond time-scale. This finding can be understood when considering the following facts. Firstly, the biologically relevant fluid phase of the bilayer is characterized by the intrinsic presence of dynamic fluctuations. Thus, the appropriate description for the positions of atoms in lipids is that of broad statistical distribution functions and the membrane surface by cannot be considered as "flat". Secondly, the location of the ensemble of chromophores is characterized by a distribution along the *z*-axis of the membrane. Thus, at a certain time, some of the chromophores might face an environment characterized by a large amount of "bulk" water molecules and thus monitor ps or even sub-ps relaxation kinetics. On the other hand, a significant part of the chromophores might be located closer to the hydrophobic part of the membrane and thus, as explained later in this abstract, probe solvent relaxation kinetics on the nanosecond time-scale.

SR in the headgroup region probed for example by 6-propionyl-2-dimethylaminonaphthalene (Prodan), 6-lauroyl-2-dimethylaminonaphthalene (Laurdan), or 6-hexadecanoyl-2-(((2-(trimethylammonium)ethyl)methyl)amino)naphthalene chloride (Patman) in PC-bilayers is purely a nanosecond process and in all three cases almost monoexponential[2]. The resulting SR times are 1.0 ns, 1.7 ns, and 1.7 ns for Prodan, Laurdan, and Patman, respectively. The observation that an "ultrafast" component is missing indicates that there is no "bulk" water present in the environment of the chromophore of those dyes. The direct influence of the chemical composition of the headgroup on the solvent relaxation characteristics indicates that the chromophores are surrounded by hydrated functional groups of the phospholipid molecules[3].

SR within the hydrophobic backbone region has been monitored by a set of n-(9-anthroyloxy)stearic acids (n-AS)[2]. Again, SR is occurring on the ns time scale. For example, the relaxation time assigned to the SR for 9-AS is about 4.0 ns[2]. In summary, we observe a slowing down of SR when starting from bulk water (τ_r in sub-ps domain), passing the external interface (τ_r in sub-ns domain) and the headgroup region (τ_r in ns domain), and finally reaching the hydrophobic backbone (τ_r is equal several ns) of the bilayer.

In the lecture an up-to-date overview on the biological applications and physical understanding of SR in biomembranes will be given.

The Center for Complex Molecular Systems and Biomolecules is supported by the Czech Ministry of Education, Youth and Sports via grant number LN 00A032.

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SYNTHESIS, RELAXOMETRIC and IN VIVO MAGNETIC RESONANCE IMAGING (MRI) STUDIES OF NOVEL Gd^{3+} COMPLEXES AS POTENTIAL MRI CONTRAST AGENTS

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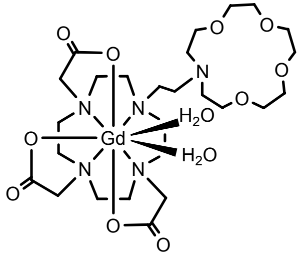
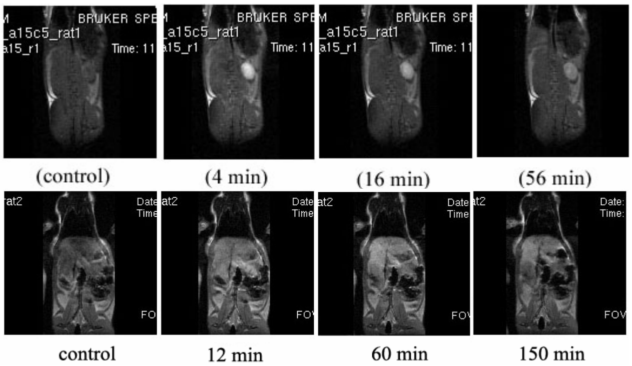
Magnetic Resonance Imaging (MRI) is a powerful diagnostic technique which allows one to obtain images of tissues and organs. The presence of paramagnetic contrast agents (CAs) in MRI causes a dramatic enhancement of water proton relaxation rates, and plays an important role in dealing with the biological assessments in intact living organisms at the level of cells and molecules. As the new generation of CAs, besides the satisfactory thermodynamic stability and kinetic inertness, they also should provide high relaxivity and tissue/organ specificity *in vivo*.



GdL1

Fig. 1. Molecular structure of **GdL1** with two inner-sphere coordinated water molecules

Regarding all the factors, neutral Gd^{3+} complexes of macrocyclic DO3A derivatives with pendant functional groups possess the best qualifications. In this work, Gd^{3+}-DO3A derivatives modified with crown ethers were designed and synthesized, moreover, its relaxometric and *in vivo* MRI studies prove that **GdL1** is a very hopeful MRI contrast agents with the advantages such as high relaxivity, outstanding renal and hepatic MRI intensity enhancements, and especially the organ specificity to liver parenchyma.



(control) (4 min) (16 min) (56 min)

control 12 min 60 min 150 min

Fig. 2. Schematic structure of **GdL1**, and MR images of the rat showing the kidney (up) and liver (low) before (control) and after the administration of **GdL1** (0.1 mmol/kg)**.**

We gratefully acknowledge financial support from the Hong Kong Research Grants Council and the University of Hong Kong. This work was also supported by the Area of Excellence Scheme of the University Grants Committee (Hong Kong).

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TOWARD ORDERED NANOPOROUS PLATFORMS FROM SELF-ASSEMBLING ORGANIC 'BUILDING BLOCKS'

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Ordered nanoporous platforms are key targets due to their diverse applications including 'smart' electronic noses[1], drug delivery vehicles[2], ultrahigh-density magnetic storage devices[3], catalytic scaffolds[4], and flow-through reactor membranes[5]. Despite extensive scientific exploration, there is currently no rapid and modular approach to fabricate these highly ordered, multi-scale systems that couple molecular level control with macroscopic tailorability. For example, functional group transformations within templated nanopores would permit diverse modifications of macroscale properties in a prompt and controlled fashion.

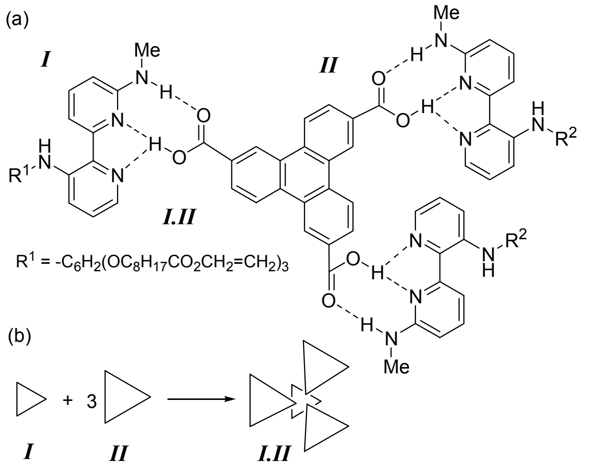

Fig. 1. Self-assembly of building-blocks into ***I.II*** complex. (a) Complementary hydrogen-bonding interactions are shown (b) Corresponding illustration portraying C_3 symmetric nature of complexation

To provide a general and modular methodology, we have synthesized organic 'building-blocks' ***I*** and ***II*** (a bipyridine triacrylate derivative and a triphenyltricarboxylic acid derivative, respectively)(Fig. 1). Building-blocks ***I*** and ***II*** are programmed to self-organize into supramolecular discotic liquid crystals via complementary H-bonding interactions (***I.II*** complex). These liquid crystal constructs, which are comprised of photoactive acrylate moieties, can be cross-linked at 254 nm forming rigid macromolecular structures (Fig. 2). Subsequent etching of the central triphenyltricarboxylic acid core **II**, affords highly ordered nanoporous scaffolds.

All results will be disclosed in more detail in this presentation.

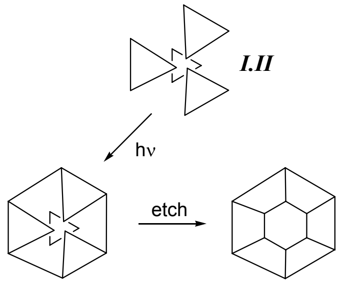

Fig. 2. Formation of hexagonally close-packed nanoporous matrix

Acknowledgements to Royal Society for University Research Fellowship, and University of Edinburgh for funding.

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DIRECTIONAL PHOTOINDUCED ENERGY AND ELECTRON TRANSFER IN METALLOCYCLODEXTRIN ASSEMBLIES

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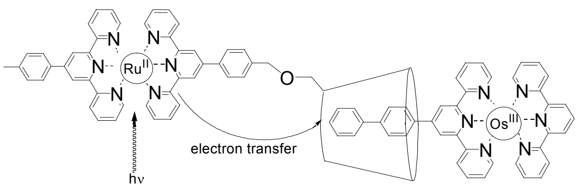
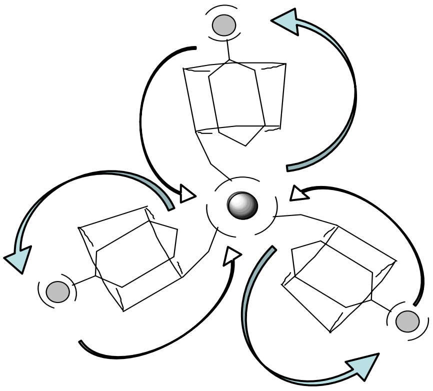
Cyclodextrin "bucket" shaped molecules are employed to assemble photo- and electro-active metal units to non-covalent wires *in aqueous solutions*. Metallo-cyclodextrins with appended photoactive ruthenium centres are prepared *via* two basic approaches, the first involving appendage of the metal centre to the bottom of the cyclodextrin cup **(1).** Metal-metal communication *via non-covalent bonds* has been established using time-resolved fluorescence spectroscopy.

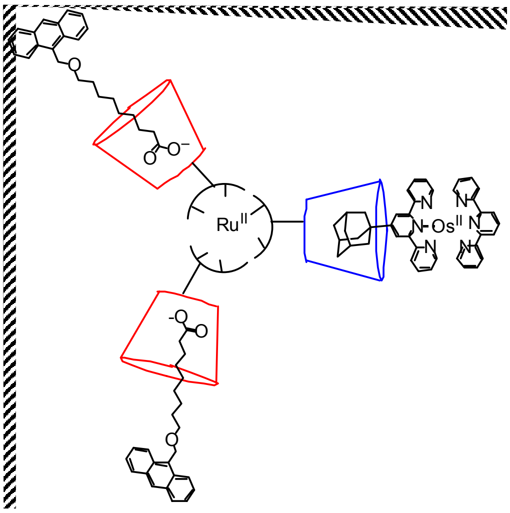


[Ru(β-CD-ttp)(ttp)]$^{2+}$ **(1)** - [Os(biptpy)(tpy)]$^{3+}$

The second approach uses metal centres to assemble more than one cyclodextrin around the luminescent centre. A ruthenium tris-bipyridine core is assembled in the **(2)**. In this system the ruthenium core acts either as energy acceptor or energy donor.



(2)



(3)

Photoinduced energy transfer is demonstrated between metal centres assembled in water by the ruthenium cyclodextrin leading to a two-way communication system, depending on the choice of the metalloguest.

Directional two step energy transfer has been demonstrated in a cyclodextrin system formed by different size cyclodextrins **(3)**.

The choice of the guest and the cyclodextrin size lead to energetic and directional control of the photoinduced process.

We thank EPSRC, The Leverhulme Trust and the Royal Society for funding.

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LIGAND DESIGN FOR LUMINESCENT LANTHANIDE COMPLEXES: FROM DNA RECOGNITION TO SENSING

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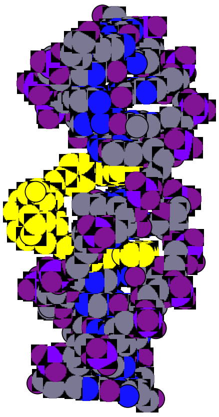
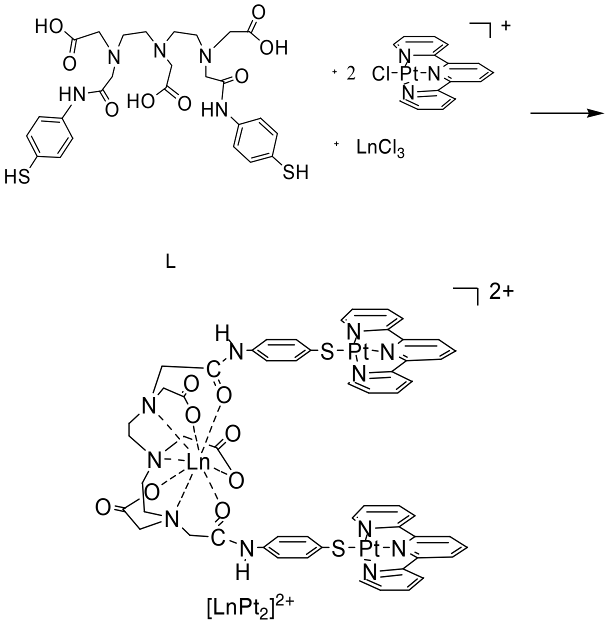
Using molecular shape for the functional control of multicomponent systems is one of the challenges in the field of supramolecular chemistry. We are interested in the controlled assembly of lanthanide supramolecular architectures and their luminescent probe function in participation in sensing schemes, interaction with biomolecules, or light conversion systems.

Luminescent Ln-Pt$_2$ metallohairpin complexes have been developed and their intercalative recognition with DNA has been demonstrated with linear dichroism spectroscopy. The heterotrimetallic complexes were formed in one-step reaction, by assembly of a derivative of a DTPA bisamide, a platinum terpyridine unit and the lanthanide salt (Scheme 1).

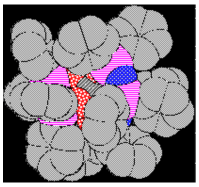
The metallohairpin complexes bear a neutral lanthanide moiety and two positively charged platinum containing intercalating units. The Nd(III) analogues are luminescent in the near infra–red and this near IR luminescence is retained upon binding to DNA.



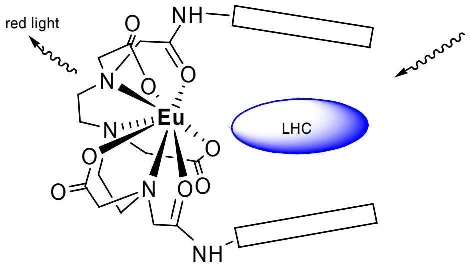
The DNA recognition was demonstrated by linear dichroism spectroscopy. The linear dichroism spectra suggested that the complexes bind perpendicular to the DNA helical axis confirming intercalative recognition accompanied by dramatic stiffening of DNA, which suggests bis-intercalation of the complex.



Scheme 1. Formation of heterometallic Ln complexes.



One ligand design involves the assembly of ligands around lanthanide ions using either steric crowding or replacement of water molecules to control the coordination sphere around the ion. Imidodiphosphinate ligands have been used to wrap around lanthanide metal ions forming a hydrophobic shell. Red and green emitting luminescent lanthanide complexes have been prepared with long lived lanthanide luminescence.



Lanthanide sensors based on bisamides of diethylene triamine pentaacetic acid have been designed by two approaches: (a) controlled formation of a ternary complex modulating the lanthanide coordination, and (b) modification of the light harvesting center (LHC) to induce secondary interactions with the arms of the polycarboxylate ligand. Luminescence studies that demonstrate sensing by the two approaches will be presented. Such systems may find analytical applications in the development of clinical assays and biomolecule labelling.

We thank EPSRC and the RSC for funding.

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SUPRAMOLECULAR CLUSTERS FROM COORDINATION CHEMISTRY: NANOSCALE CHIRAL FLASKS

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Supramolecular assemblies found in nature, such as ferritin and protein viral coats, have inspired our design, synthesis, evaluation and use of nanometer scale molecular flasks formed through self-assembly. Based on labile metal-ligand interactions, we have designed nanoscale container molecules. The validity and utility of rational design and computer modeling has been proven by preparing a number of structures in which a single, discrete product is formed and extra metal or ligand components are excluded (Fig. 1)[1,2].

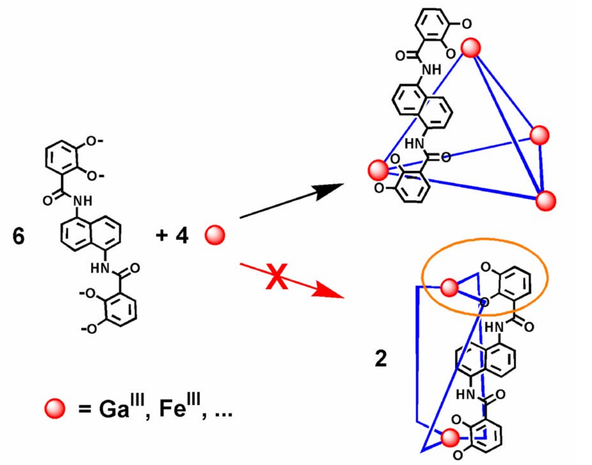

Fig. 1. Synthesis of an M_4L_6 tetrahedral assembly. Formation of other structures than the tetrahedron is not observed

The metal-ligand assemblies are highly negatively charged and very water-soluble. However, they have hydrophobic interiors of about 0.5 nm^3 that strongly and selectively encapsulate hydrophobic cationic guests. Because of *tris*-bidentate chelation at the metal vertices and mechanical linkage between the metal vertices, these clusters are homochiral and resolvable. The structure, once resolved, can retain its chirality indefinitely[3]! Replacement of components of the cluster after such resolution shows a structural memory of the assembly with the optical activity continuing unabated[4].

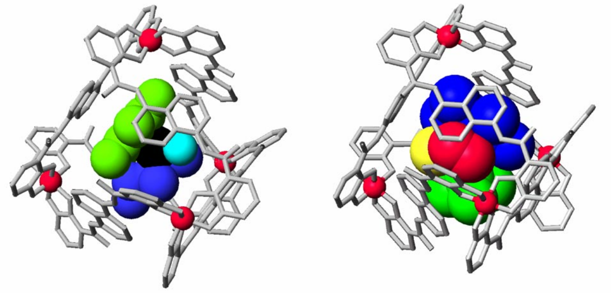

Fig. 2. Molecular models of $[Cp^*Ru(2\text{-ethylbutadiene})(H_2O)^+ \subset Ga_4L_6]^{11-}$ (left) and $[Cp^*Ir(PMe_3)(Me)(ethylene)^+ \subset Ga_4L_6]^{11-}$ (right)

The encapsulation of reactive organometallic complexes leads to host-guest assemblies with reactivity properties determined by both, host and guest. Monocationic ruthenium sandwich complexes show a high affinity for the M4L6 supramolecular assemblies and exhibit altered reactivity once encased5. Chiral ruthenium half-sandwich complexes of the general formula [Cp*Ru(diene)(L)]+ also proved to be suitable guests and their encapsulation into the chiral cavity proceeds with high degrees of enantioselection (up 85:15 dr)6. The recognition process proves to be highly shape and size dependent. Encapsulation of [Cp*Ir(PMe3)(Me)(ethylene)]+ resulted in a host-guest complex with rather remarkable reactivity. The activation of aldehydic C-H bonds occurs at the enclosed iridium center but the host-structure dictates the size and shape selectivity of the reaction. Aldehydes that are small enough to encapsulate and approach the iridium center are activated, while aldehydes too bulky to enter the cavity do not undergo C-H bond activation7. This represents a new mode of controlling and harnessing reactivity.

Currently, we are pursuing the identification of catalytically active host-guest complexes. In addition, we are exploring the possibility of utilizing the supramolecular structure as the catalyst itself.

The authors would like to thank Drs. Anna V. Davis and Robert M. Yeh for their seminal contributions and helpful discussions. This research is supported the NSF (KNR) and DOE (KNR and RGB).

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MULTI-PORPHYRINIC POLY-URIDINE

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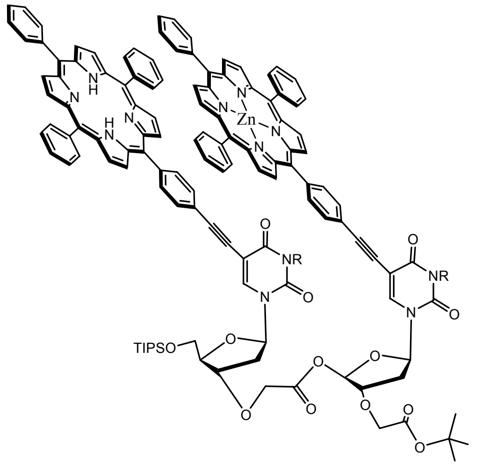
In photosynthetic systems, the solar energy is collected by pigment molecules attached to the light harvesting complexes. In these units, the chlorophylls are held in a favored spacing and orientation by fairly short α-helical polypeptides[1]. When a photon hits one of the chlorophylls, the absorbed energy spreads extremely rapidly to the others until the reaction center is reached. The extraordinary efficiency of the energy migration over long distances with minimal loss of energy is ascribed to the favored spacing and orientation of the chlorophylls which are held in an appropriate parallel orientation.

Beyond the control of the structure of multi-chromophoric arrays, monitoring the spatial orientation of the chromophores in artificial light harvesting devices is a challenge of growing interest. Indeed, multi-porphyrinic arrays attract more and more attention, for the synthesis of artificial light harvesting complexes[2] as well as for the elaboration of photonic and electronic wires[3]. Molecular architecture with light harvesting porphyrins represent attractive building blocks for the fabrication of functionalized nanostructured systems[1,2].



We report herein the preparation of a nucleoside/porphyrin conjugate[4] based on the stepwise functionalization of uridine at both C-3’ and C-5’ positions of the ribose and at the C-5 position of the uracil nucleic base. Iodation at C-5 allows coupling of the desired porphyrin. The protecting groups of both O-3’ and O-5’ alcohols were chosen in order to allow selective cleavage, which is necessary to build up an oligomer of defined sequence of porphyrins (metallated or not). Modeling studies show that a parallel orientation of the porphyrins can be expected in such oligomers. An efficient quenching of the luminescence of the Zn(II) porphyrin was observed in the dimer represented above, which was attributed to an energy transfer towards the free base porphyrin.

By this design we are approaching new nano-sized molecules and supramolecular aggregates by controlled covalent or supramolecular synthesis.

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SYNTHETIC, ION-CONDUCTING TRANSMEMBRANE CHANNELS

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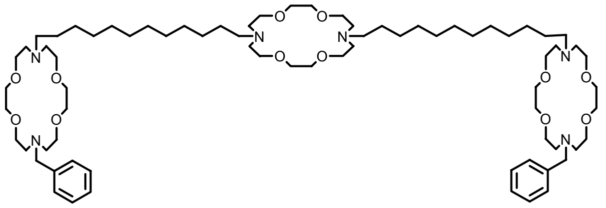
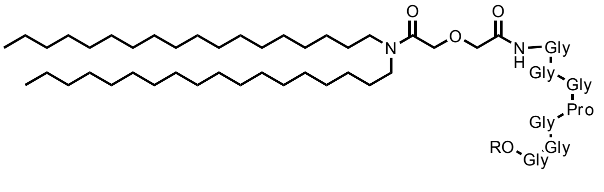
Macrocyclic polyether compounds are excellent cation binders and their complexation behavior has been extensively studied during three decades. We have incorporated macrocycles into structures that we have developed for use as model cation-conducting transmembrane channels. These compounds transport H^+, Na^+, K^+ through phospholipid membranes. Sodium transport has been assessed by dynamic ^{23}Na-NMR methods and proton flux has been measured by fluorescence techniques. Sodium and potassium fluxes have been determined in certain cases by bilayer clamp methods in phospholipid bilayers. Hydrophile channels are currently thought to form water- and sodium-filled pores through the bilayer. Issues such as position in the bilayer, conformation, and biological activity will be discussed.

Chloride selectivity represents a second goal and challenge of the synthetic ion channel project. Results describing the design, synthesis, and characterization of an anion-selective channel will also be presented. In this case, the synthetic system involves an amphiphilic heptapeptide. An example of hydraphile channels is shown below at the left, below. A representative of the chloride-transporting, heptapeptide channels is shown at the right.





IMPORTANCE OF THE DISPERTION INTERACTIONS FOR CYCLOBIS(PARAQUAT-*p*-PHENYLENE) BASED MOLECULAR “SHUTTLES“.

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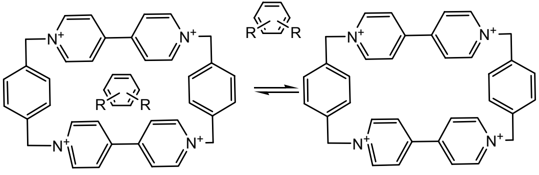
Inclusion complexes of cyclobis(paraquat-*p*-phenylene) and various aromatic molecules in their neutral and oxidized form have been studied at LMP2/6-311+G**//BHandHLYP/6-31G* level of theory which represents the highest level theoretical study to date for these complexes.



Calculations show unambiguously that the origin of stability of cyclobis(paraquat-*p*-phenylene) inclusion complexes with donor molecules is dispersion interaction which can contributes up to 100 % to the binding. This finding is in agreement with all available experimental data. The binding energies calculated in this paper are based on the highest level calculation performed to date for these types of systems and they are believed to be very close to genuine binding energies. Since dispersion interactions are very distance sensitive, shape of guest molecule play an important role. Although, dispersion stabilization represents the main contribution to the stabilization energy, guest molecules having dipole moment impart additional stability to the complex due to electrostatic interaction. The oxidation of guest molecule not only decreases stability of supramolecular complex but creates extremely powerful repulsive potential (around 200 kcal/mol) between guest and host molecules leading to its complete dissociation. Since the oxidation of guest molecule creates such a strong repulsion between guest and host molecules, therefore, low oxidation potential and high polarizability of guest molecule are the keys features to take into account when designing a molecular “shuttle” based on cyclobis(paraquat-*p*-phenylene) host.

This research was carried out with the support of grant IX-102404/14 from DGAPA.

MACROCYCLIC VS. DENDRIMERIC EFFECT; A DFT STUDY

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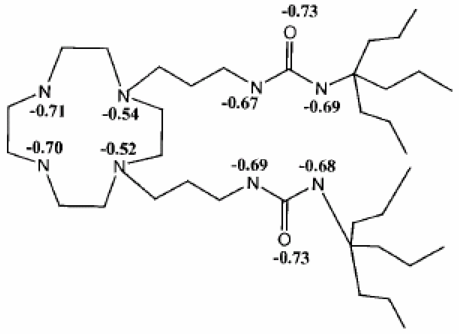
Crown compounds[1] have had a great importance as cation binders[2] as well as agents for extraction and transport processes. These macrocyclic compounds also play an important role in the molecular recognition area, in view of the fact that they impose a significant degree of order. Hence, the macrocycles themselves provide high level of preorganization; however, what could happen if further attachment of pendant complexing donor groups, like functionalized-dendrimeric groups, were considered into the whole structures? Can such a level of preorganization increase even more? It was observed previously that there is a cooperative effect when several functionalities are present in supramolecular assemblies like dendrimers connected to macrocyclic systems[3] and, depending on the flexibility of the involved branches and the functional groups attached to them, it can be possible to obtain a sum of several noncovalent interactions in a collective fashion. Dendrimers by themselves, as macrocycles, have shown interesting host– guest properties.

In the present study[4], macrocycles up to 15 members with different heteroatoms (N, O, and S) and dendrimeric functionalized branches were assembled, resulting in unique “collective” supramolecular hosts with several active sites for transition metal ions complexation (scheme 1). The nature of the interactions between these kinds of systems and metal ions of the first transition series (Fe, Ni, Cu, Zn) was evaluated by calculations of the binding energies at the B3LYP/LACVP* level of theory, resulting in a preference of metal ions for macrocyclic cavity in terms of complexation; however, there is a favorable contribution in energy due to the cooperative effect of dendrimeric branches (DBs) in the inclusion process by means of long-range interactions between metal ions and the heteroatoms present in DBs. The capability of macrocycles as host entities is related to: (1) the compatibility in orbital symmetry between host and guest molecules; (2) the cavity dimensions and the negative charge inside; and (3) the hardness–softness affinity between host and guest molecules.



Scheme 1. Example of supramolecular system

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PREPARATION AND CHARACTERIZATION OF NEW COMPLEXES BASED ON THE INTERACTION OF CU(II) IONS WITH IONIC LIQUIDS

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Room temperature ionic liquids have been considered as "green" recyclable alternatives to the traditional volatile organic solvents because of their chemical and physical properties. They are liquid at room temperature with virtually no vapor pressure, are stable towards air and moisture and have high solubility power.

The present study deals with the behavior of monovalent and divalent copper salts dissolved in ionic liquids based on N,N dialkylimidazolium cations.

UV-vis spectra of $CuSO_4$, $CuCl_2$ and $CuBr_2$ dissolved in 1-butyl-3-methylimidazolium tetrafluoroborate ($BmimBF_4$) show an absorption peak at 295 nm and a shoulder at 407 nm. The values of ε at 295 nm are: 3450, 6010 and 9990 $M^{-1}cm^{-1}$, respectively, whereas the values at 407 nm are: 1800, 2940 and 3620 $M^{-1}cm^{-1}$, respectively. The UV-vis spectra of $CuCl_2$, and $CuBr_2$ dissolved in 1-butyl-3-methylimidazolium hexafluorophosphate ($BmimPF_6$) show only a peak at 250 nm, while for $CuSO_4$ it is shifted to 260 nm. The values of ε for these three compounds are: 10400, 22270 and 900 $M^{-1}cm^{-1}$, respectively.

CuBr and CuCl dissolved in $BmimBF_4$ absorb at 240 nm with an ε of 2964 and 2510 $M^{-1}cm^{-1}$, respectively. CuBr and CuCl dissolved in $BmimPF_6$, absorb at 245 nm. The values of ε for these two compounds are: 5010 and 5150 $M^{-1}cm^{-1}$, respectively.

ESR spectra of Cu(II) ions in $BmimBF_4$ and $BmimPF_6$ are typical of a d^9 ion in an almost planar configuration. Cu(I) in $BmimBF_4$ is ESR silent indicating that Cu(I) is stable probably due to complexation with the ionic liquid. However, Cu(I) in $BmimPF_6$ is probably oxidized by dissolved oxygen as evidenced by an ESR spectrum typical of a Cu(II) complex.

The electrochemistry at a glassy carbon electrode of the copper (II) ions dissolved in the ionic liquids was investigated by cyclic voltammetry. Preliminary results for $CuCl_2$ dissolved in $BmimBF_4$ show two quasi- reversible waves with $E_{1/2}$ of 0.36 and 0.08 V vs. Fc/Fc^+ while only one wave with $E_{1/2}$ of 0.19 V vs. Fc/Fc^+ is observed for $CuCl_2$ dissolved in $BmimPF_6$.

MOLECULAR RECOGNITION IN CHEMOMECHANICAL POLYMERS – ON THE WAY TO REAL MOLECULAR MACHINES

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The molecular machines known until now require for communication to the outside world additional physical devices, including power supply, etc. In contrast, introduction of supramolecular binding sites into flexible polymers allows for the first time to translate selective molecular recognition events directly into large macroscopic motions, leading to functions such of artificial muscles. Uptake of effector compounds from the aqueous surrounding can lead to fully reversible size expansions of such polymer films by up to 2000% in volume. Different hydrogels are used as basis, including those containing polyamines and lipophilic alkyl or aryl groups as host components; these show different expansions for a large variety of effectors. Inorganic anions lead to sizeable motions, as do different nucleotides such as AMP, UMP, GMP, TMP, or various aromatic substrates. The kinetics of the size changes obey first order rate laws, with half life times of minutes; these can be diminished by increasing the surface to volume ratio of the polymer particles.

The macroscopic dimension changes can dramatically depend on the presence or two effector compounds in the surrounding medium, either with negative or with positive cooperativity. These dimension changes occur if two different effectors are present within a narrow concentration range, thus providing for the first time a chemically induced macroscopic logical XOR or AND gate. This applies also to the strong dependence of the effector-driven expansions on the pH value of the surrounding solution.

Selective interactions of the covalently attached supramolecular polyamine binding sites with transition metal ions show large macroscopic size changes by simultaneously added metal chelators, aminoacids and peptides. The new strategies open the way to new molecular machines, actuator, drug delivery and sensor systems, which are triggered by selective chemical stimuli from the environment.

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DYNAMIC COMBINATORIAL LIBRARY FOR THE SYNTHESIS OF DIFFERENT OPTICALLY ACTIVE POLYAZAMACROCYCLES

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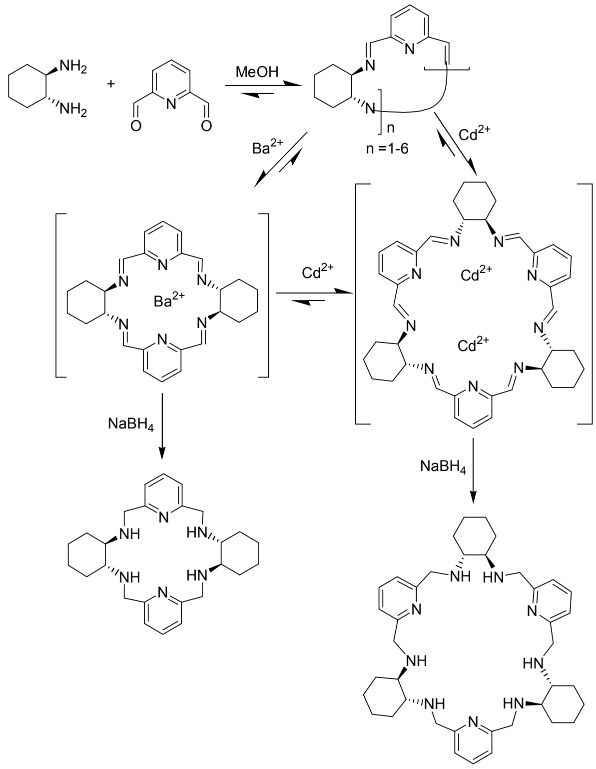
Dynamic combinatorial library (DCL) concept is becoming a useful tool for the discovery and isolation of new host and guest compounds[1].

Herein we describe the amplification of two different receptors from the same DCL of macrocyclic imines, by templating of Ba^{II} or Cd^{II} metal salts. The equilibrium mixture is frozen by simple in situ reduction of the C=N bonds, which leads to optically active poliazamacrocycles in a one-pot methodology. These compounds are interesting because of their applications in chiral molecular recognition[2].

We studied the thermodynamic template effect and the structure of the final compounds by a combination of ESI-MS, UV and NMR spectroscopy, and X-ray crystallography techniques. A cooperative molding effect for the Cd ion-templated process was observed and a second level of molecular diversity, based on the imine/α-methoxyamine equilibrium, was demonstrated.



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AMPEROMETRIC AND SPECTROPHOTOMETRIC BEHAVIOR OF AN IMMOBILIZED ENZYME ON ELECTRODE PREPARED BY LAYER-BY-LAYER ASSEMBLING

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Construction of nano-interfaces between biomolecules and electrodes are current interest to develop bio-electronic molecular devices. While various types of techniques for immobilization of enzymes onto the electrode surface through covalent or non-covalent interactions have been reported up to the present time[1,2], more convenient and efficient methods to create the bio-electronic interface have been still required. In the present work, we prepared an enzyme-modified electrode by employing the alternate layer-by-layer assembling technique[3,4], and characterized the catalytic behavior by means of amperometry and spectrophotometry.

Onto a self-assembled monolayer of 3-mercaptopropionic acid prepared on a gold electrode of quartz crystal resonator, a cationic and an anionic polymer were assembled alternatively, and followed to attach an enzyme on the surface. The assembling process was monitored by quartz crystal microbalance. When NADH-dependent lactate dehydrogenase was used as the enzyme, electrochemical response of the enzymatic reaction was effectively observed depending on the combination of the cationic and anionic polymer. The catalytic conversion of pyruvate to L-lactate on the electrode in the cell was monitored simultaneously by amperometry and spectrophotometry. The present enzyme-modified electrode maintained the catalytic activity more than 1000 hours.

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SUPRAMOLECULAR ASSEMBLY OF CERASOMES ON DNA TEMPLATES

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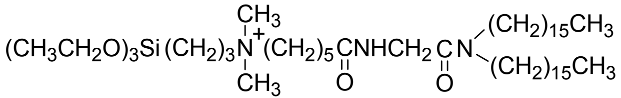
Recently, we have developed a novel organic-inorganic hybrid "Cerasome" as a biomembrane model[1]. The Cerasome is the lipid bilayer vesicle like liposome, but its surface is covered with siloxane networks like silica. One of the characteristics of the Cerasome is its enhanced morphological stability as compared with the conventional liposomes and synthetic bilayer vesicles[2]. Thus, three-dimensional assemblies of vesicular nanoparticles as multi-cellular models can be achieved by integration of the Cerosomes on solid substrates[3,4]. We report here on the formation of vesicular assembly of the Cerasomes with DNA in aqueous media.

The Cerasome derived from an organoalkoxysilane lipid ***I*** performed as a cationic vesicle with a hydrodynamic diameter of ca. 40 nm under physiological conditions, as confirmed by dynamic light scattering and zeta-potential measurements. In the presence of a double-strand DNA, the Cerasomes were self-assembled on the DNA template with keeping the vesicular shape. Such behavior was observed by means of transmission electron microscopy, differential scanning calorimetry, dynamic light scattering measurements, and so on. On the contrary, cationic bilayer vesicles formed with the conventional lipids were not able to keep the vesicular shape to induce fusion after the vesicular aggregation. The present supramolecular assembly of the Cerasomes with DNA is interesting in the light of development of the artificial multi-cellular systems and/or the vectors for gene delivery.



$$(CH_3CH_2O)_3Si(CH_2)_3\overset{+}{N}(CH_3)_2(CH_2)_5\underset{O}{\overset{\|}{C}}NHCH_2\underset{O}{\overset{\|}{C}}N\begin{matrix}(CH_2)_{15}CH_3\\(CH_2)_{15}CH_3\end{matrix}$$

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SYNTHESIS OF A NEW OPTICALLY ACTIVE POLYAMINE

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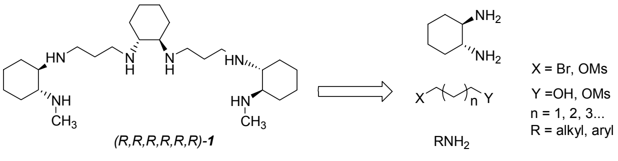
The developing of new organic receptors able to specifically interact with different kinds of anionic species has attracted much attention both in chemical and biological fields[1]. Many important molecules in living systems are anionic at phisological pH. Another important characteristic of biomolecules is that they usually present chirality, which often determines their function. However, the desing and synthesis of new receptors for optically active polyanions is a difficult task by conventional chemical methods[2]. Here we report the preparation of a new linear optically active polyamine which could be used in molecular recognition of biologically interesting chiral anions, such as oligopeptides and oligonucleotides, it also may have potential as DNA delivery and transfection agents[3].



We have obtained the polyamine *(R,R,R,R,R,R)-**1*** in a high yield following a strategy based on conventional reactions of protection and alkylation of amines. It has the conformational rigidity in order to effectively transfer the chirality to the anion in the supramolecular complex.

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SELF-ASSEMBLED GRAPHITIC NANOTUBES

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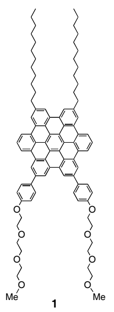
Hexa-*peri*-hexabenzocoronene (HBC) is well known for its propensity to assemble into large aggregates because of strong intermolecular pi-pi stacking forces[1]. We have used this force, in combination with an amphiphilic effect, to assemble discrete high aspect ratio nanotubes composed of the HBC molecules[2].

The self-assembled graphitic nanotubes consist of a bilayer ribbon formed by interdigitation of the dodecyl chains of the unsymmetrically substituted HBC. The curved 2D wall of the tube comes about as a result of a helical coiling of the bilayer ribbon. The tubes can be isolated in high yield from the self-assembly solution by filtration. SEM showed the fibrous structure while TEM revealed the tubular nature of the self-assembly. The helical nature of these nanotubes was discovered by self-assembly of the tubes in the presence of water.



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TIFF (LZW) decompressor
are needed to see this picture.

Scheme 1. Chemical structure of the HBC derivative and a TEM image revealing its nanotubular structure

The nanotubes consist of the electroactive HBC unit. Thus, they could be oxidized by reaction with an appropriate electron acceptor (nitrosonium tetrafluoroborate) and the electrical conductivity of the tubular self-assembly was determined by positioning a single tube across nanogap electrodes. The tubes were found to be semi-conducting following oxidation.

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INTERMOLECULAR COMMUNICATION ON LIPID BILAYER MEMBRANE. SWITCHING OF ENZYMATIC ACTIVITY BY A LIPID SIGNAL

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Biomembranes are natural supramolecular assemblies on which functional connection of membrane-bound biomolecules such as receptors and enzymes affords wireless communication networks as signal transduction systems. Much effort has been devoted to architect supramolecular assemblies artificially on lipid bilayer membranes, by mimicking the biological systems[1,2]. Recently, we have shown that functional connection between molecular recognition by an artificial receptor and signal amplification by an enzymatic reaction can be achieved on synthetic bilayer membranes[3,4]. We also revealed that the enzymatic activity on the lipid membrane was synchronized with activation of a lipid signal through molecular recognition[5].

We report here the specificity of the molecular recognition of a lipid signal with the signal activator species and its consequence in efficiency of the enzymatic activity switching. Phosphatidylethanolamines as a lipid signal, embedded in the synthetic bilayer vesicle formed with a cationic peptide lipid, exhibited marked selectivity for various pyridoxal derivatives as a signal activator to form the imine complex having strong metal-binding affinity. Thus, the activity of a membrane-bound enzyme such as lactate dehydrogenase was controlled by synchronizing with the molecular recognition of the lipid signal in the presence of copper(II) ions as a mediator.

This work was financially supported by the Japan Society for the Promotion of Science, Grant-in-Aid for Scientific Research (A), 15205022, 2004.

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BIPHENYL MODIFIED THIOUREAS FOR CARBOXYLATE SENSING

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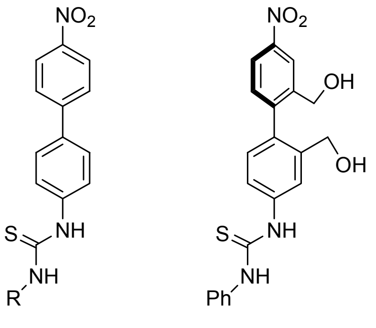
The design and synthesis of neutral anion receptors are of current interest in host-guest chemistry[1]. Carboxylate anions play an important role in many chemical and biological processes. In biological systems, anion recognition is very often achieved *via* hydrogen bonding by highly pre-organized proteins. Thioureas are excellent hydrogen bond donors for carboxylates and there are several recent examples in the literature of thiourea-based synthetic carboxylate receptors[2]. On the other hand, the design of a sensor requires the attaching of an appropriate signaling unit to the receptor to convert the binding process to an optical signal. In this context we would like to report the synthesis of three neutral receptors based on thioureas with appending 4'-nitrobiphenyl moieties, and the recognition and sensing properties for carboxylates.

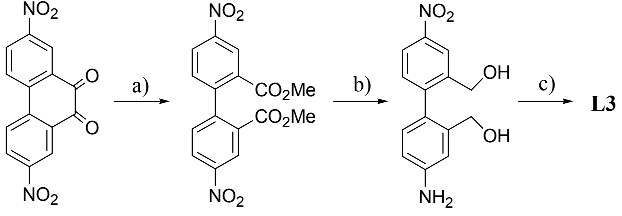
Receptors **L1** and **L2** were synthesized by reaction of phenylisothiocyanate or ethylisothiocyanate and 4-amino-4'-nitrobiphenyl. Ligand **L3** was obtained in several steps starting from 4,4'dinitrophenanthrenequinone **1** as shown in Scheme 2.



L1 R = Ph
L2 R = Et
L3

Scheme 1. Carboxylate receptors **L1**-**L3**

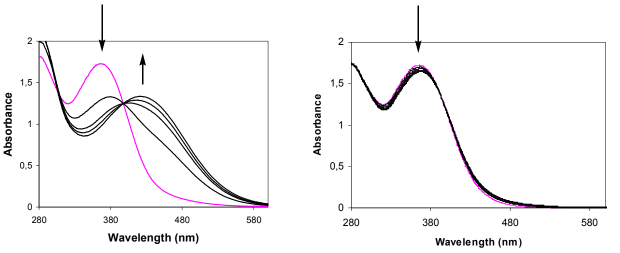
Binding constants of **L1**-**L3** for various carboxylates (acetate, hydroxyacetate, benzoate and salicilate, all as tetramethyllammonium salts) were calculated by ^{1}H NMR titration. As expected, all the receptors form 1:1 complexes with the carboxylate anions.



1 **2** **3**

Scheme 2. Synthesis of **L3**. (a) 1) H_2O_2, AcOH; 2) MeOH, H_2SO_4. (b) 1) $LiBH_4$, THF; 2) Na_2S, H_2O, Na_2CO_3. (c) PhNCS.

The effect of carboxylates on the UV-vis absorption and fluorescence emission spectra of the ligands was investigated in DMSO for **L1** and in MeCN for **L2** and **L3**. For **L1** the most significant changes in UV-vis spectra are observed in the presence of aromatic carboxylates (benzoate and salicilate), while the addition of acetate or hydroxyacetate produces a very slight response (see Scheme 3). The presence of substituents at the 2,2'- positions of the biphenyl moiety has strong influence on the UV-vis spectra of **L3**, which show an hypsochromic shift in the λ_{max} probably due to the higher dihedral angle between the aromatic rings adopted by this ligand in order to reduce steric hindrance.



Scheme 3. Changes in UV-vis spectra of **L1** titrated with benzoate and acetate (as Me_4N^+ salts) in DMSO.

With respect to the fluorescence spectra, **L1** shows again the most significant changes: addition of 1 equiv. of AcO^- to **L1** results in three-fold fluorescence enhancement. A very different behaviour is observed in the fluorescence spectra of **L1** as compared to **L2** and **L3**. While addition of carboxylates to **L1** gives rise to an enhancement of the fluorescence emission, the spectra of **L2** in the presence of carboxylates show a decrease in the fluorescence intensity.

Ministerio de Ciencia y Tecnología and Ministerio de Educación y Cultura of Spain are gratefully acknowledged for a Ramón y Cajal contract (P. G.), a predoctoral grant (G. R.-M.) and project PPQ2002-00986.

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SYNTHETIC RECEPTORS BASED ON VITAMIN B_{12} SYNTHESIS AND APPLICATION

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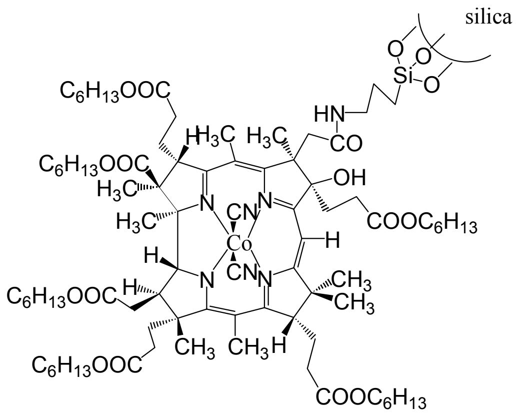

Fig. 1 Structure of covalently bonded synthetic receptor based on vitamin B_{12}

Novel synthetic and modified natural receptors based on vitamin B_{12} have been prepared. Their covalent linking to silica allow the study of their interactions on the boundary between two phases. One interesting application of such immobilized receptors is in the separation science. Our receptor modified silicas have been used as stationary phases for high-performance liquid chromatography. Interaction with a number of aromatic and polyaromatic compounds will be discussed.

Grants CEZ: MSM 223400008 of the Ministry of Education, Youth and Sports of the Czech Republic, and grants 203/02/0933, 203/02/0420 from Grant Agency of the Czech Republic, and EU grant QLRT-2000-02360 supported the work.

LANTHANIDE COMPLEXES WITH A *p-tert*-BUTYLCALIX[8]ARENE FITTED WITH PHOSPHINOYL PENDANT ARMS

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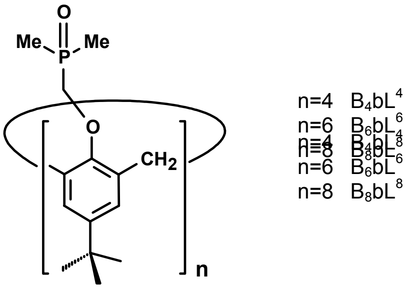
Calixarenes are amenable to easy functionalization at both their narrow and wide rims, which makes them attractive hosts in supramolecular and coordination chemistry. Calixarenes fitted with phosphorous-containing pendant arms are used in catalysis, in the design of chemical sensors and in separation processes. The major goal of this project is the development of new calixarene-based receptors for the separation of actinides (An) and lanthanides (Ln) as well as for various analytical and heavy-metal recycling processes.

As a follow up of our work on Ln complexes with B_4bL^4 and B_6bL^6,[1, 2] the new wide-rim functionalized macrocycle, 5,11,17,23,29,35,41,47-octa-*tert*-butyl-49,50,51,52,53,54,55,56-octakis(dimethylphosphanylylmethoxy)calix[8]arene, (B_8bL^8, see Scheme), has been synthesized. Our purpose is to unravel the influence of the larger flexibility of the calix[8]arene framework, and larger denticity, on both the stoichiometry and stability of the complexes with trivalent lanthanides. We report the structural and photophysical properties of both B_8bL^8 and its 2:1, 1:1, and 1:2 (Ln:L) complexes in the solid state (IR, luminescence) and/or in solution (mass spectrometry, ^{1}H- and ^{31}P-NMR, UV-vis absorption and metal-centred luminescence). We aim at understanding the principles underlying the metal ion recognition by this macrocyclic host and evaluating the potential of B_8bL^8 as extraction agent.



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SUPRAMOLECULAR ASSEMBLIES DERIVED FROM AMIDE DENDRONS

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Recent advances in self-assembly of dendrimers or dendrons provide a unique methodology to create supramolecular nanomaterials[1-2]. Previously, we have reported on the formation of thermoreversible dendritic organogels, and the formation of lamella or columnar hexagonal arrays in dry state depending on the structures of the dendron building blocks[3]. In this work, we introduced aromatic junctions such as biphenyl, naphthoxy, and isopropylidenediphenoxy groups into the bridge unit of the dimmer of amide dendrons to investigate the self-assembly characteristics not only in organic media but also at the solid-liquid interface.

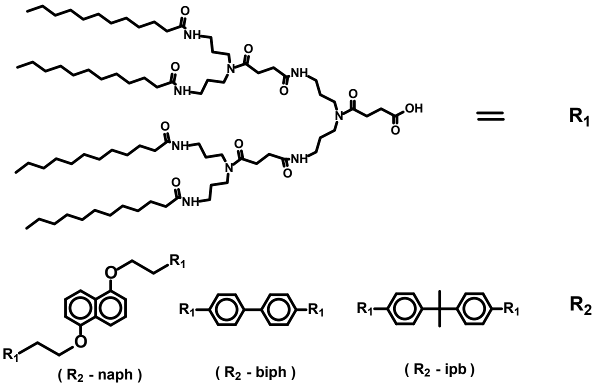

Fig. 1. General structure of amide dendrons.

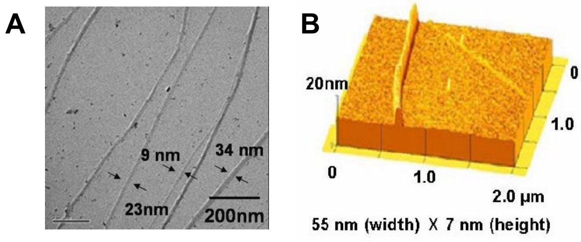

Fig. 2. TEM and AFM images of self-assembled nanoribbons of B-naph at the solid-liquid interface.

Dimeric dendrons with aromatic core bridges formed thermoreversible organogels in methylene chloride, THF, octanol, and decanol. The dry gel from **R_2-naph** in octanol showed well-defined nanoribbons, while the other two gels of **R_2-biph** and **R_2-ipb** from octanol revealed relatively short stands of fibrils in TEM images. The XRD measurements of **R_2-naph** gel revealed a lamellar structure with interlamellar spacing of 70 +. The TEM images and the XRD results of the dry gel from **R_2-naph** suggest that **R_2-naph** forms lamella nanoribbons. In contrast, **R_2-biph** exhibited the hexagonal columnar structure with the column diameter of 63 +. However, **R_2-ipb** did not form gels in octanol and decanol. This can be attributed to the sterically crowded kink structure of the central isopropylidenebiphenyl group which could hinder the packing process of the dendritic building blocks. These results obviously indicate that the core bridging units are critical not only for the formation of supramolecular assemblies of the dendritic dimers but also for determination of the nature of the supramolecular structure.

In addition, we investigated the self-assembly characteristics of these dimeric dendrons at the solid-liquid interface. First, we prepared a dilute (0.1 wt %) solution of **R_2-biph** in octanol. However, this dilute solution did not form any gel. On the other hand, exposition of the solid surface such as carbon-coated copper grid or silicon wafer to the dilute octanol solution (0.1 wt %) of **R_2-biph** brought about well-defined nanostacks on the surface with the width ranging from ~10 nm to ~40 nm (Fig. 2 (A)). The AFM images in Fig. 2 (B) also confirmed that each nanostack is uniform in width with a length spanning several micrometers. The height of the nanostack is 7 nm in Fig. 2 (B). Considering the stretched dimension of **R_2-biph** (84 +) in the direction of long molecular axis, **R_2-biph** building blocks are lying parallel on the solid surface and a uniform number of dimer building blocks are stacked in the vertical and the transverse direction. These results suggest that dimeric dendron **R_2-biph** forms self-assembled lamellar structure on the surface with a uniform number of lamellar layers in inplane direction, and the building blocks are assembled together to form a lamellar stack with a uniform width and a length of several microns.

The design of dimeric dendrons with functional elements at the bridge moiety would provide a unique route to the supramolecular nanomaterials with functional elements in an organized state.

This work was supported by Korea Research Foundation (2003-041-C00242).

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NEW REACTIONS OF DISINTEGRATION OF CALIXARENE CYCLE UNDER ACTION OF ELECTROPHILIC REAGENTS

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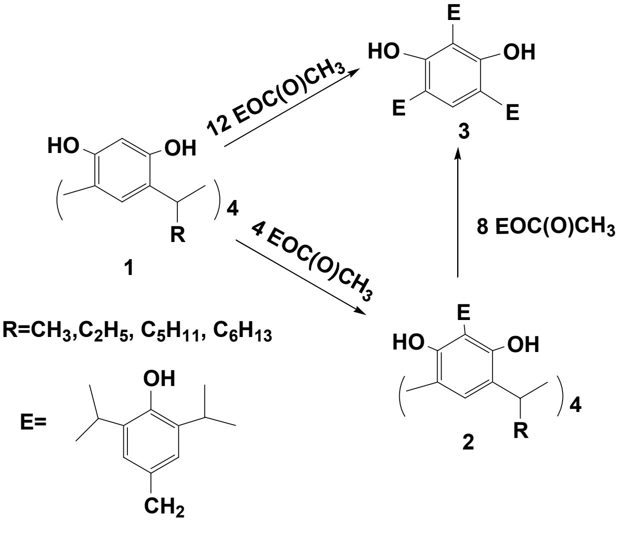
Reactions of calix[4]resorcinoles ***1*** with 1,2,4-triazin-5(2*H*)-ones[1] and 3,5-di-tert.butyl-4-hydroxybenzyl acetate were investigated for the first time. It is established, that depending on reagents ratio and acid nature used two directions are realized to form products of electrophilic substitution ***2*** or products of disintegration of calixarene cycle ***3***.



The structure of obtained products was proved by IR, NMR ^{1}H, ^{13}C spectroscopy methods and MALDI TOF mass spectroscopy, X-ray analysis.

This work was supported by Russian Foundation for Fundamental Research (grant № 02-03-33037) and the International Bureau of the Federal Ministry of Education and Research (BMBF, RUS 02/034).

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UNUSUAL REACTIONS OF RESORCIN, 2-METHYLRESORCIN WITH PHOSPHORUS CONTAINING VINYL ESTERS, α,β - AMINOALDEHYDES AND THEIR ACETALES

ALEXANDER R.BURILOV[a], **YULIA M. VOLODINA**[a], **ALMIR S. GAZIZOV**[a], **IRINA R. KNYAZEVA**[a], **MICHAIL A. PUDOVIK**[a], **WOLF D. HABICHER**[b], **INGMAR BAER**[b] **and ALEXANDER I. KONOVALOV**[a]

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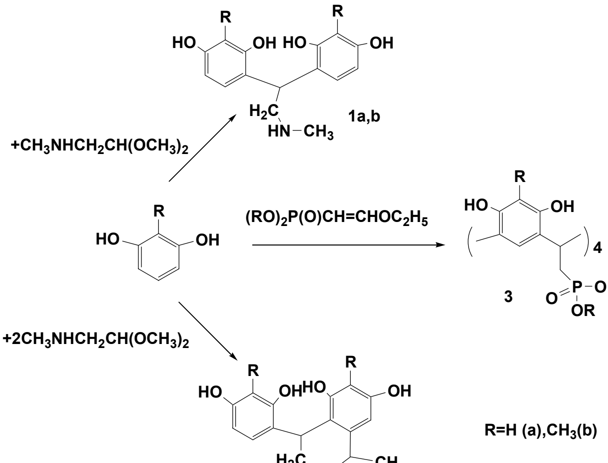
We have investigated the condensation reactions phosphorus containing vinyl esters, of various α,β-aminoaldehydes and their acetales with resorcin and 2-metylresorcin in order to obtain new types of calix[4]resorcinols. It has appeared, that in this reaction either new linear polyphenols ***1a,b***, ***2b*** or calix[4]resorcinols ***3*** are formed depending on the structure of α,β-aminoaldehydes and their acetales.



The structure of obtained products was proved by IR, NMR ^{1}H, ^{13}C spectroscopy methods and MALDI TOF mass spectroscopy, X-ray analysis.

This work was supported by Russian Foundation for Fundamental Research (grant № 02-03-33037) and the International Bureau of the Federal Ministry of Education and Research (BMBF, RUS 02/034).

NOVEL PORPHYRINS WITH ATTACHED MULTIPLE PENTAMETHINIUM CONJUGATED SYSTEMS

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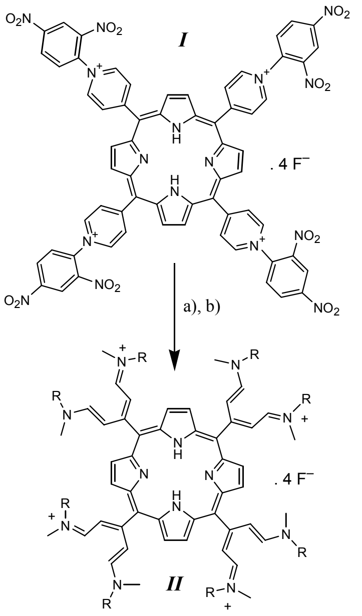
The search of novel porphyrinoid derivatives represents one of the leading themes of supramolecular and medicinal chemistry[1]. Here we present new functionalized porphyrins bearing pentamethinium systems at the *meso*-positions. These compounds were synthesized starting from tetrakis(4-pyridyl)porphyrin and 2,4-dinitrofluorobenzene. The subsequent pyridine ring opening reaction of tetrakis(dinitrophenylpyridinium) intermediate ***I*** with excess of secondary amines gave water soluble products ***II*** (Scheme 1). Novel porphyrins are currently tested for application in PDT, showing interesing results.



Scheme 1. a) 2,4-dinitrofluorobenzene, 130 °C, 4 days;
b) MeNHR

Authors gratefully acknowledge financial support of the Ministry of Education of the Czech Republic (MSM 223400008) and Eur. Comm. grant project QLRT-2000-02360 and GACR grant project Nr. 203/02/0420, 203/030900 and 309/02/1193

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INTERACTION OF SELF-ASSEMBLED HYDROPHOBIC COMPOUNDS WITH PROTEINS: SPECIFIC RECOGNITION OF AGGREGATED MOLECULES

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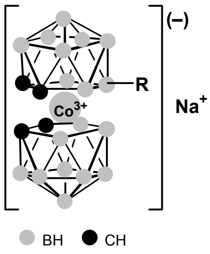
Hydrophilic environment causes formation of self-assembled hydrophobic aggregates in solutions of hydrophobic compounds. Although it may seem this process to be non-selective, we can make it specific by designing recognition parts of molecules. In this way we can utilize this phenomenon in monitoring of small molecules' interaction with proteins, as recently demonstrated for concanavalin A[1]. A general sensing mechanism involves the specific interaction of aggregated and primarily nonfluorescent labels with the target protein, label deaggregation, site specific binding and fluorescence signaling. Here we firstly describe self-assembled aggregates of several bioactive carborane clusters ***I*** and porphyrin ***II*** in water solutions, their properties and specific/non-specific interactions with target proteins monitored by fluorescence spectroscopy, quasielastic light scattering (QELS) and atomic force microscopy (AFM).



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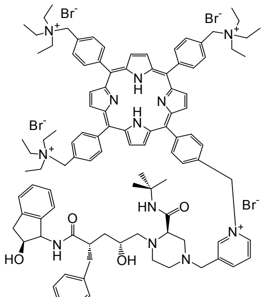

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Authors gratefully acknowledge financial support of the Ministry of Education of the Czech Republic (MSM 223400008) and Eur. Comm. grant project QLRT-2000-02360 and GACR grant project Nr. 203/02/0420

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OLIGOPYRROLE-BASED ANION BINDING AGENTS

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Anion recognition is an important problem that is of critical relevance to a range of processes, both biological and abiological. In this presentation, the use of protonated expanded porphyrins and neutral calix[n]pyrroles as receptors for anions will be reviewed. Synthetic methods leading to the preparation of calix[n]pyrroles, where $n > 4$, will be highlighted, as will be preparative work that leads to the preparation of so-called “expanded calixpyrroles”, including those based on bipyrrolic precursors. Related work that has led to the production of new three dimensional, “cryptand-like” systems will be detailed. Also discussed will be recent work with open chain pyrrole-based receptors, including dipyrrolylquinoxalines and analogues that show promise as colorimetric sensors. Finally, the results of studies designed to highlight the potential utility of oligopyrrolic systems in a variety of application areas, ranging from separation science and-self assembly, to medicine, will be presented. In the latter context, a particular emphasis will be placed on sapphyrin as a possible new class of anticancer agents and as a receptor for the radioactive pertechnetate anion.

For a list of publications, including both specialized research articles and more generalized reviews relevant to this topic, the reader is kindly requested to access URL: www.cm.utexas.edu/sessler/

This work was supported by the National Institutes of Health, the National Science Foundation, The Department of Energy, Pharmacyclics, Inc. and Kraft Foods, Inc.

SYNTHETIC PORPHYRINOID CHEMISTRY

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In recent years, novel porphyrinoids have emerged as promising functional molecules, which possess unprecedented properties that are not common for normal porphyrins. We report two porphyrinoids; 1) *meso-meso* linked porphyrin arrays and 2) *meso*-aryl substituted expanded porphyrins. Among many molecular modules used as construction elements of molecular wires, porphyrins are one of the most attractive building blocks owing to their favorable photophysical and electrochemical properties. Treatment of a zinc(II) 5,15-diarylporphyrin with Ag(I)-salt in $CHCl_3$ led to the formation of *meso-meso* directly linked diporphyrin and triporphyrin[1]. This coupling reaction has been extended to three-dimensional windmill and grid-like porphyrin arrays[2,3], a discrete 128-mer with a molecular length of 0.1 μm in its straight form[4], poly(5,15-porphyrinylenes)[5], 1,3-phenylene-bridged cyclic 12-mer with a diameter[6] of 36-38 Å, and directly linked porphyrin rings[7]. In most cases, the direct *meso-meso* linkage result in considerably large but not conjugated electronic interactions between the neighboring porphyrins owing to perpendicular conformations[8,9]. This property is quite suitable for the use as synthetic light-harvesting antenna[10].

Directly *meso*-β linked diporphyrins were prepared by one-electron oxidation of copper(II)-, nickel(II)-, and palladium(II)-porphyrins[11]. Furthermore, we explored the multiply linked diporphyrins; *meso*-β doubly linked diporphyrins, *meso-meso*, β-β doubly linked diporphyrins, and *meso-meso*, β-β, β-β triply linked diporphyrins[12,13]. Among these, the triply linked diporphyrin displays the strongest interactions as evinced by its extremely red-shifted Q-band like absorption. The oxidation of end-phenyl capped *meso-meso* linked zinc(II) porphyrin arrays with DDQ and $Sc(OTf)_3$ enabled the extension of the triply linked array up to the 12-mer (porphyrin tapes)[14]. Extensive electronic delocalization in the porphyrin tapes is remarkable in terms of their extremely red-shifted absorption bands which reach in the infrared. The optical HOMO-LUMO gap is estimated to be extremely small, ca. 0.43 eV for the porphyrin tape 12-mer, encouraging their use as a molecular wire.

Another topic is the chemistry of *meso*-aryl substituted expanded porphyrins that can be regarded as real homologues of *meso*-aryl substituted porphyrins in terms of the conjugated cyclic π-system with alternate arrangement of pyrroles and methine carbon atoms[15]. These expanded porphyrins are prepared by modified Rothemund-Lindsey reaction of pyrrole and pentafluorobenzaldehyde[16,17,18]. Structures, optical and electrochemical properties, and metallation behaviors of expanded porphyrins including *N*-fused pentaphyrin, hexaphyrin, heptaphyrin, octaphyrin, nonaphyrin, decaphyrin, and dodecaphyrin will be discussed in comparison to those of porphyrins[19]. An interesting example is the thermal splitting reaction of bis-copper(II) [36]octaphyrin(1.1.1.1.1.1.1.1) into copper(II) porphyrin[20].

This work is supported by CREST (Core Research for Evolutional Science and Technology) of Japan Science and Technology Agency and Grant-in-Aid from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

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SOL-GEL ENCAPSULATION OF OLIGOSACCHARIDES FOR CHIRAL SEPARATION BY CAPILLARY ELECTROPHORESIS AND ELECTROCHROMATOGRAPHY

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Chitosan, gelatin and other oligosaccharides containing chiral centres can be used as enantiomeric selectors. For encapsulation of the selector was used a promising sol-gel method. The method is based on hydrolysis and condensation of suitable alkoxides (TMOS, TEOS). During sol-gel formation, the viscosity of the solution gradually increases as the sol forms a rigid, porous network - the gel. An inner capillary wall was activated (subsequently by NaOH, H_2O, HCl and H_2O) and after that was filled up with gel. Amino acids (Trp, Tyr) and some pharmaceuticals were chosen as the analytes. Influences of various conditions (selector concentration, gel drying, separation buffer etc.) will be discussed.

Grants CEZ: MSM 223400008 of the Ministry of Education, Youth and Sports of the Czech Republic.

A NEW ENTRY TO PORPHYRIN-TRISGUANOSINE CONJUGATES AS SELECTIVE RECEPTORS FOR GUANOSINE-5´-MONOPHOSPHATE

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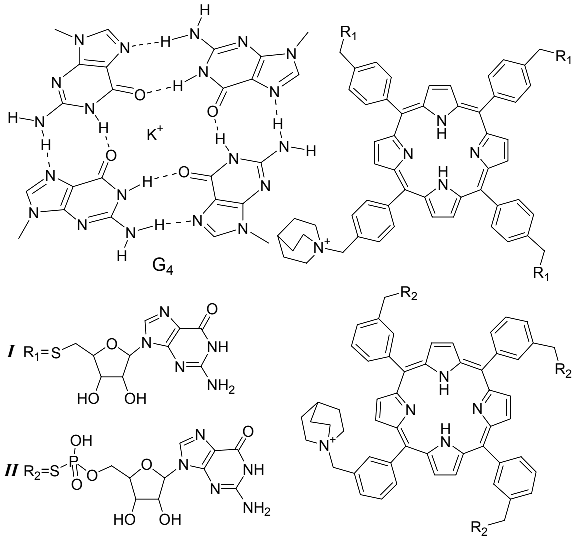
Guanosine is one of the base nucleotides found in the human genome and regulates of cellular functions in nearly all cell types. Its ability to form a self-complementary hydrogen-bonded square quartet (G_4) was used for the design of the novel receptors ***I***, ***II*** for guanosine-5´-monophosphate (GMP).



Receptor design is based on the preparation of water soluble porphyrin derivatives containing three guanosine moieties (G_3), which would be able to form a G_4 with fourth guanosine in the form a GMP. A porphyrin ring was chosen as an efficient platform that can stabilize the G_4 formation by π-π stacking. Its strong absorption allows easy monitoring of the binding process. The receptor has a positive charge for binding of a phosphate group of GMP. Moreover, the positive charge improves receptor polarity, that is a requisite for binding studies under physiological conditions.

The binding properties of desired receptors were then studied by several spectroscopic methods and ITC experiments. The reaction sequence for the preparation of ***I***, ***II*** as well as binding affinity to nucleotides will be presented.

Authors gratefully acknowledge financial support of Grant Agency of the Czech Republic (grant Nos. 203/02/0420, 203/02/0900, 309/02/1193). This work is also supporting by Hans-Fischer Foundation.

BIS- AND TRIS-TRÖGER'S BASE DERIVATIVES – NEW BUILDING BLOCKS IN SUPRAMOLECULAR CHEMISTRY

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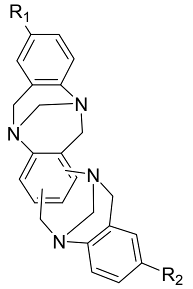
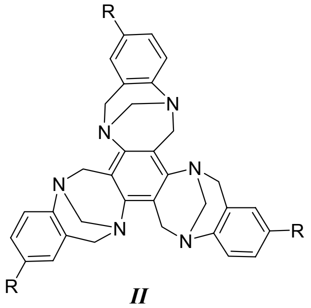
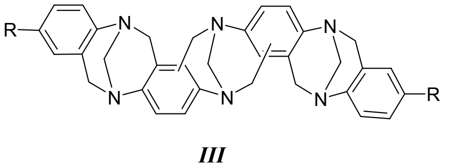


I



II



III

The methanodiazocin bridge of Tröger's base (TB) integrated into receptor design gives a chirality and rigid V-shape. Recently, Pardos's[1, 2] and our[3] group described formation of bisTB systems ***I***. From supramolecular point of view, their *syn* configuration ("boat-like") is more attractive than *anti* ("chair-like") because corresponds to molecular tweezers. Extension into oligoTB systems (for example trisTB ***II***) can afford isomers with "dish-like" configuration resembling calixarenes[3].

The new findings in preparation of new oligoTBs ***I-III*** as well as determination of their configuration will be covered in our contribution.

Authors gratefully acknowledge financial support of the Ministry of Education of the Czech Republic (MSM 223400008) and Grant Agency of the Czech Republic (grant No. 203/03/D049).

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PREPARATION OF CHIRAL HETEROCYCLIC TRÖGER'S BASE DERIVATIVES CONTAINING *N*-METHYLPYRROLE UNIT

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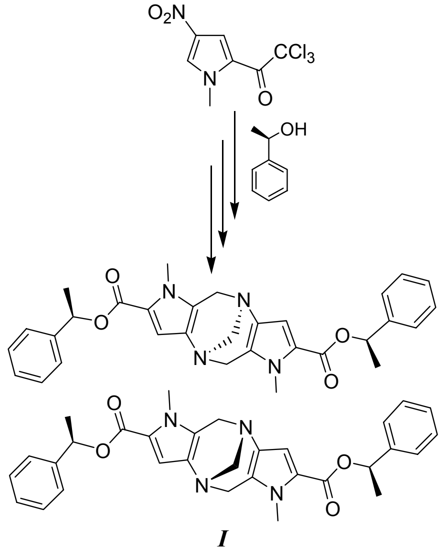
Tröger's base (TB) structure motif is used for the construction of chiral receptors. Moreover, some heterocyclic TB analogues enantio-specifically interact with DNA[1]. Our contribution to this area has involved development of TB derivatives of natural antibiotics, as distamycine and netropsine analogues[2]. Chiral preparation of these compounds is based on the separation of diastereoisomeric mixture of ***I*** obtained using optically pure 1-phenylethanol (Scheme 1).



I

Scheme 1: Preparation of diastereoisomeric mixture of *N*-methyl-pyrrole TB derivative

Although no chiral induction was observed at the formation of **I**, the acid catalyzed crystallization of diastereoisomeric mixture **I** gave only one diastereoisomer of **I**. The synthetic sequence of **I** as well as resolution conditions will be more described.

Authors gratefully acknowledge financial support of the Ministry of Education of the Czech Republic (MSM 223400008) and Grant Agency of the Czech Republic (grant Nos. 203/02/0420, 203/02/0933, 309/02/1193).

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METAL COORDINATION CHEMISTRY OF N-CONFUSED PORPHYRINOIDS

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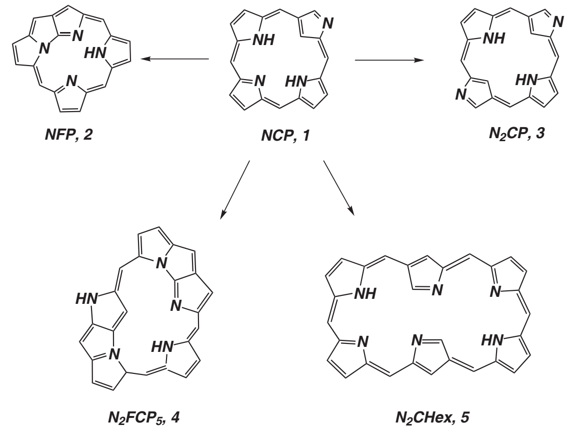
Synthesis and metal coordination chemistry of porphyrin analogues have been attracting considerable attention due to the structural diversity and their potential for a variety of applications.



Since the discovery of *N*-confused porphyrin (**1**)[1,2], we have been synthesizing a series of *N*-confused analogues, such as *N*-fused porphyrins (**2**)[3], multiply *N*-confused porphyrins (**3**)[4], and corresponding expanded ones (**4, 5**)[5,6], which all exhibit unique properties that are different from normal porphyrins. Remarkably high affinity for halide anions, efficient photosensitization for singlet oxygen, near IR absorption and emission, formation of self-assembled hydrogen bonding network, etc., these features owe largely to the *confused* pyrrole ring(s) introduced in the macrocyclic core. In this presentation, the metal coordination chemistry of *N*-confused porphyrinoids will be highlighted.

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PORPHYRIN ASSEMBLIES FOR CHEMICAL SENSORS DEVELOPMENT

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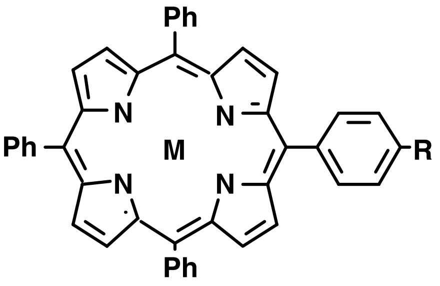
The preparation of thin films of porphyrin derivatives is of great interest due to their potential in material science and for, among others, optical, chemical sensors application, and solid-state synthetic hemoproteins[1].

In the course of our studies, devoted to the achievement of solid state chemical sensors, composed of arrays of quartz crystal microbalances (QCM), we developed a protocol based on the deposition of self-assembled monolayers (SAMs) of porphyrin diads bearing elements of chirality[2]. This system presents promising features in terms of enantiomeric recognition towards chiral volatile organic compounds. This challenging aspect is remarkably important for the application to real matrices. One of the most compelling characteristics influencing the properties of porphyrin monolayers is, undoubtedly, the geometry and orientation of the deposited mesostructure. Several strategies can be followed for the preparation of porphyrin layers with controlled features. Construction of SAMs on gold, for example, lead to assemblies with different electrocatalytic properties, depending on the specific orientation of the macrocycles on the gold surfaces. Langmuir-Blodgett (LB) or Langmuir-Schaefer (LS) techniques have been employed for the fabrication of chiral porphyrin films. Very recently, it has been reported that the geometry of the absorbed thin layer of porphyrin derivatives can be controlled by depletion interactions. Furthermore, deposition of well defined porphyrin nanorods aggregates have been reported to occur from acidic solutions of water-soluble porphyrin derivatives, or by successive complementary coordination of imidazole to cobalt ion. Peculiar "wheel-like" structures have been obtained by controlled evaporation of porphyrin derivative solutions. Porphyrin deposition on quartz, induced by UV irradiation, has also been reported, showing that the photophysical properties of the resulting mesoaggregate can be tuned by changing the central metal ion of the tetrapyrrolic macrocycles. In this paper we report on a new, efficient method of porphyrin layer deposition, by simply dipping a hydrophobic, silanised, glass surface into an aqueous porphyrin solution.

We observed the formation of porphyrin thin film deposition during our studies on the aggregation behaviour of several amphiphilised porphyrin derivativatives (Chart 1) such as [5-(4-(3-trimethylammonium)propyloxyphenyl)-10,15,20-triphenylporphyrin] chloride (Scheme 1. **1H$_2$**). UV-vis spectra of **1H$_2$** aqueous solutions (μM concentration) showed the formation of porphyrin J-type aggregates gradually on going from pure ethanol to a water-ethanol (90/10 v:v) solvent mixture.

UV-vis spectral changes and concomitant molecular deposition spontaneously occurs with time, from the aqueous solvent mixture. Microscope glass slides, with silanised hydrophobic surface, were used as substrate. Dipping the slides into an aqueous solution of **1H$_2$** ($2.x10^{-6} \div 7.5x10^{-5}$ M; $H_2O/EtOH$ 9:1, v:v) resulted in the deposition of porphyrin aggregates, as evidenced by the typical yellow coloration of the glass surfaces.

Remarkably, the obtained films are characterised by good mechanical stability and, as witnessed by several spectroscopic techniques, by an evident degree of order. AFM image showed the presence of regularly oriented porphyrin suprastructures, extending regularly over the whole micrometric scale with about 450 nm width.



1H$_2$: R = $OCH_2CH_2CH_2NMe_3Cl$; M = 2H
1MnCl: R = $OCH_2CH_2CH_2NMe_3Cl$; M = MnCl
1Co: R = $OCH_2CH_2CH_2NMe_3Cl$; M = Co
2H$_2$: R = $O(CH_2CH_2O)_2CH_2CH_2OH$; M = 2H
3H$_2$**:** R = CO_2H; M = 2H

Scheme 1.

We studied the potential exploitation of these layered films for sensing applications, for the detection of analytes in liquid or gaseous environment.

The free base porphyrin thin films have been tested for the detection of heavy metal ion in water solution, while Zn or Co derivatives were exploited for the detection of volatile organic compounds.

The sensing performances of these films are particularly promising and the results obtained will be presented and discussed.

The author thanks FISR-MIUR, project SAIA for funding.

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DYNAMIC COMBINATORIAL CHEMISTRY: NEW OPPORTUNITIES FOR MOLECULAR RECOGNITION AND CATALYSIS

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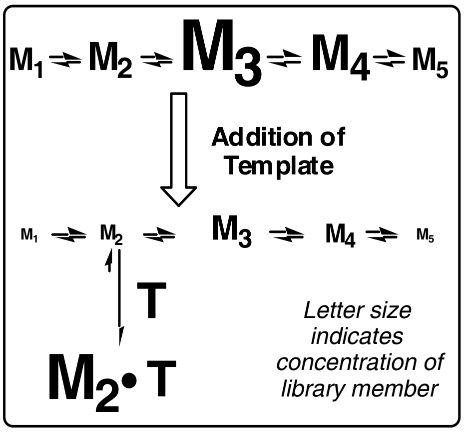
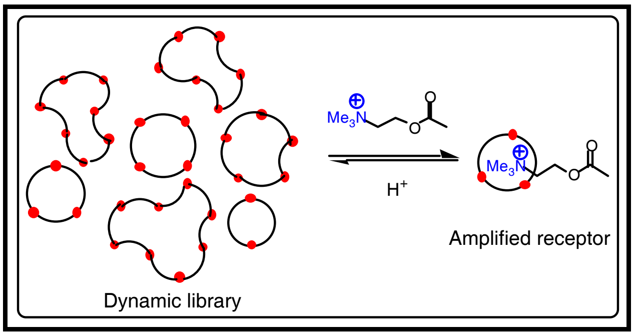
Dynamic combinatorial chemistry (DCC) is a new approach to finding ligands for biological receptors, and new synthetic receptors for guest templates. If that guest is a transition state analogue for a given reaction, the amplified receptor might be a catalyst for that reaction. DCC is the synthetic chemists' equivalent of biology's evolution and selection approach, and is the solution state equivalent of the molecularly imprinted polymer approach.



A combinatorial library consists of many members ($\mathbf{M_1}$.......$\mathbf{M_n}$) each of which contains two or more building blocks (*A*, *B*, *C*......) arranged in a particular way. In a dynamic combinatorial library the connections between building blocks are reversible, continuously being made and broken. The composition of a dynamic library will be dependent on its environment as shown: addition of a template **T** that selectively binds one member will bias the equilibrium towards that member.



Covalent synthesis of macrocycles under such thermodynamic control offers proof reading of 'incorrect' structures and access to the optimum receptor for any given guest template. We have explored several reactions including hydrazones and disulfide exchange; building blocks include peptides, porphyrins and aromatics.

The templated amplification of numerous receptors and a catalyst from dynamic libraries will be presented.

There are some key references for further information. Reviews on dynamic combinatorial chemistry and reversible covalent chemistry[1-3], amplification of receptors and a catalyst from a dynamic combinatorial library of disulfides in water[4-5], Molecular amplification of an acetylcholine receptor from a pseudo-peptide dynamic combinatorial library[6-7], cyclic pseudo-peptide receptors for M^+ from hydrazone dynamic combinatorial libraries[8-9], simultaneous, selection, amplification and isolation of a pseudo-peptide receptor from a dynamic combinatorial library by an immobilised template[10], dynamic combinatorial libraries of metalloporphyrins: templated amplification of disulfide-linked oligomers[11], simulations of large dynamic combinatorial libraries[12-13].

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USE OF PH-SENSITIVE LIPOSOMES AS CARRIERS FOR *N*-BUTYLDEOXINOJIRIMYCIN IN B16-F1 MURINE MELANOMA CELLS

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Liposomes are used as delivery vehicle of drugs, proteins, DNA, for pharmaceutical, biochemical and cosmetic purposes. When toxic drugs are needed to be delivered, often the use of liposome-encapsulation is an alternative to reduce the required concentrations to less toxic values and minimize the side effects. Also, liposomes could be used to target specific tissue such as tumors.

Protein glycosilation in tumors such as skin cancer is believed to be different from that in normal tissues. Therefore glycosilation inhibitors like *N*-butyldeoxinojirimycin (*N*B-DNJ), an ER alpha-glucosidases I and II inhibitor, could potentially be used as anti tumor agents.

In our study we used pH-sensitive liposomes composed of DOPE:CHEMS (6:4) as drug carriers for *N*B-DNJ in B16-F1 mouse melanoma cells. We followed the enzymatic activity and the *N*-glycan structures of tyrosinase, the key enzyme of the melanin biosynthesis pathway. Our results revealed that *N*B-DNJ had a better efficiency following inclusion in liposomes as compared to the free added compound. Thus, in the presence of 50 μM of liposome-included *N*B-DNJ, tyrosinase failed to acquire *N*-glycan complex structures, and its enzymatic activity was reduced about seven fold. By fluorescence microscopy we showed that liposomes containing calcein as fluorescent marker enter the cells by endocytosis and in early stages of internalization co-localized with acidic compartments of the endocytic pathway. Three hours after internalization the liposomes content was released into the cytoplasm.

Studies are in progress to evaluate the effect of liposomes-*N*B-DNJ formulation on cells growth and morphology.

NON-COVALENT CONJUGATES OF CORROLES AND PROTEINS: EXTREMELY SIMPLE, YET VERY EFFECTIVE BIOMIMETIC SYSTEMS

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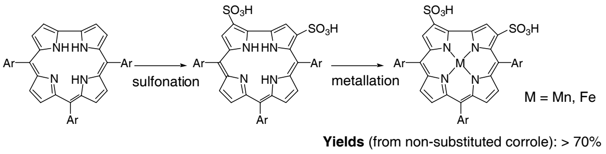
In sharp contrast to tetraarylporphyrins, triarylcorroles remained almost unknown for decades and there was no report about *any* corrole in *any* of the many applications where porphyrins play a dominant role.

New synthetic methodologies allowed for the facile preparation of more than 100 new triarylcorroles in the last 4 years and parallel investigations revealed that the corresponding metal complexes are potent catalysts for a variety of reactions. In addition, electrophilic substitution of the β-pyrrole carbon atoms was found to be an extremely facile and highly selective methodology for the synthesis of amphiphilic corroles, such as the one shown in Scheme 1.



Scheme 1. Synthesis of amphiphilic corroles

Our current emphasis is on the bis-sulfonated corrole shown in the Scheme, whose metal complexes were shown to form tightly bound non-covalent conjugates with a variety of proteins. The bioconjugated iron and manganese corroles catalyze asymmetric processes in heme-enzyme like fashion, utilizing H_2O_2 for enantioselective oxidations.

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DIVERSITY OF HOST-GUEST BINDING MODES: A SIGN TO RESIGN FROM DESIGN?

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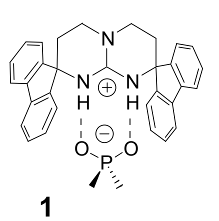
Molecular host-guest binding is uniformly visualized as a process in which 2 (or more) binding partners assemble to form a complex possessing a discernable topological and geometric arrangement - a structure. This structure represents the platform for the analysis and interpretation of selectivity and affinity features along with the delineation of suggestions for their further improvement. On this basis the famous lock-and-key picture had been cast more than a century ago and because of its simplicity and intuitive comprehensiveness has ruled the thinking about supramolecular interactions ever since. Undoubtedly the underlying principle of complementarity of the interacting interface is a true and valid reflection of the molecular situation and dominates the energetics in many examples. However, as the measurement of thermodynamic state functions Δ*H* and Δ*S* in addition to the free enthalpy of binding Δ*G* becomes more abundant the common picture of exclusively enthalpy-governed association is unfolded as an exceptional case and must be supplemented to accommodate scenarios resting on entropy production as the major source of binding free enthalpy. Whilst positive association entropies have usually been attributed as the sole cause to desolvation processes at the host-guest interface it now becomes clear that this might not be the exclusive origin.



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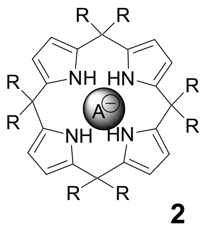

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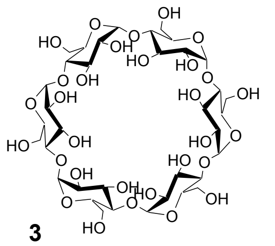

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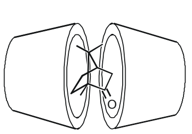

We shall present experimental arguments drawn from the host-guest binding to artificial receptors in the guanidinium **1** calixpyrrole **2** and cyclodextrin **3** series that demonstrate the participation of multiple binding modes in supramolecular complexation These results prompt consequences for the rational design of abiotic hosts.

THE [3+3] CYCLOCONDENSATION OF *trans-1R,2R*-DIAMINOCYCLOHEXANE WITH RIGID DIALDEHYDES: AN EASY WAY TO CHIRAL MACROCYCLES

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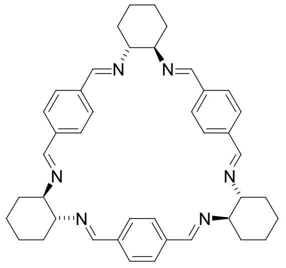
Recently, we[1] and others[2] have shown that the non-template reaction of enantiomerically pure *trans*-1,2-diaminocyclohexane with terephthaldehyde gives exclusively the product of the [3+3] cyclocondensation ***I***.



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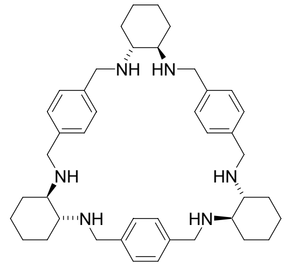

II

The effect of the diamine as well as the dialdehyde structure on the cyclisation reaction has been studied. Comparison of the solution studies using gel permeation chromatography with the composition of the solid products has given us deeper look into cyclocondensation equilibria and led us to the conclusion that the rigid rod-like dialdehydes tend to form the [3+3] macrocycles analogous to ***I*** both in solution and in the solid state. Chiral hexa-Schiff bases obtained upon the [3+3] cyclocondensation of *trans-1R,2R*-diaminocyclohexane with the rigid rod-like dialdehydes can be easily reduced to the corresponding macrocyclic hexaamines (analogous to ***II***) producing thus a novel class of useful chiral macrocyclic ligands.

Complexation studies of hexaamine ***II*** have revealed its significant selectivity for binding benzene-1,3,5-carboxylate over the positional isomers: benzene-1,2,3- and benzene-1,2,4-carboxylates. Solid state crystal structures of some new macrocycles will be discussed.

Financial support from Academy of Sciences (Z4 055 905) and Grant Agency of the Czech Republic (203/03/0087) is acknowledged.

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REDOX ACTIVE SELF ASSEMBLED MONOLAYERS DEPOSITED ONTO GOLD ELECTRODES

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The self-assembly monolayer approach , credited to Allara and Nuzzo[1,2], has opened the new possibilities for creating chemically modified substrates such as : Au, Pt, Ag, Cu, Hg, which could be applied for designing new class of sensors.

In the work presented, dipyrromethene derivatives (thiol, sulfide) have been applied for gold modification. The dipyrromethene, after binding transition metal ions such as Cu^{2+}, Ni^{2+}, Zn^{2+}, could act as the redox active monolayers[3]. This might creates the new sensing possiblity.

The characterization of SAMs has been done by: cyclic voltammetry, infrared spectroscopy and contact angles.

The response of dipyrromethene SAMs towards protons and anions selected will be presented

This work was supported by Bilateral Collaboration Flander – Poland (BIL/01/04) and Institute of Animal Reproduction and Food Research of Polish Academy of Sciences. The offering facilities by IMEC vzw, Leuven for the performing the measurements presented is gratefully acknowledged.

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QUINONO-DIAZA CROWN ETHERS AND CATENANES

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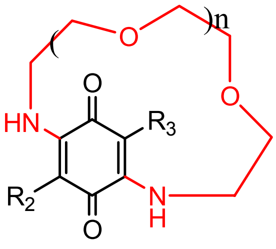
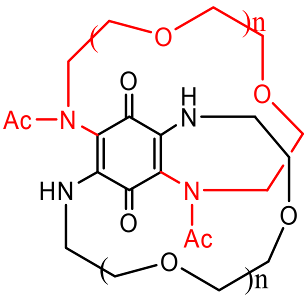
Quinone bearing macrocycles, *e.g.* geldanamycins and ansamycins are among the most potent antibiotics and antitumur agents. Quinone containing crown ethers represent a coupled system in which an electroactive quinone group is in physical proximity to an ion-binding crown ether moiety. Such a system opens exiting possibilities, offering the ability to couple a redox reaction with ion binding properties.

Host-guest complexes can be formed in which the reduced (hydroquinonic) form is a much stronger ligating donor than the neutral (quinonic) form. The two mechanisms mutually influence each other and might add to our understanding of analogous biological active compounds.

We will present our results in this field. Thus the reaction of polyoxyalkylene diamines (Jeffamine-148 and Jeffamine-192) with various 1,4-benzoquinones yield the appropriate quinonoid crown ethers (**1**) and catenanes (**2**).



(1)



(2)

In this communication, we will present the synthetic results, spectroscopic data, redox properties and single crystal X-ray structures of these monocyclic and bicyclic quinonoid derivatives.

DETECTION OF COLORLESS BIOMOLECULES WITH NOVEL SENSING AGENTS

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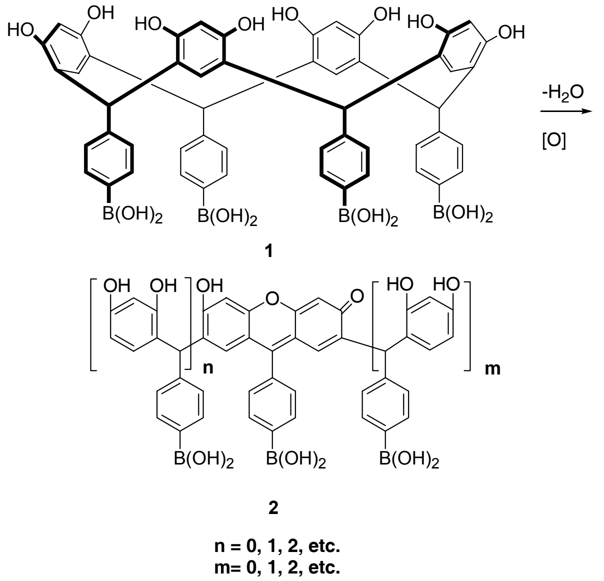
The detection of saccharides and amino acids in biological media is of great current interest for the monitoring of disease states and industrial processes. We find that solutions of tetraarylboronic acid resorcinarenes turn color upon standing or heating[1]. The macrocyclic materials form acyclic oligomers containing chromophoric xanthene moieties[2]. Our current efforts focus on modulating the colorimetric and fluorimetric properties of these and related xanthene dye materials towards the selective detection of specific biological analytes.



Scheme 1.

The spectroscopic properties of xanthenes in the presence of sugars and amino acids are due to complex formation and, in some cases, electron transfer. Selectivity for specific biomolecules can be attained in biological and aqueous media by varying the xanthene structure or detection conditions.

We find that eleven different solutions containing different sugars afford various sugar-dependent colors[1]. Additionally, color changes of solutions of neutral oligosaccharides can be easily seen[2]. We additionally apply these methods towards the fabrication of an automated post-column HPLC detection system which allows for the observation of sugar and ganglioside analytes using any common UV-vis detector[3].

We have designed simple colorimetric tests for the determination of fructose in commercial honey samples. Additionally, the detection of glucose in human blood plasma by fluorescence is possible using our materials[4]. By dual wavelength monitoring, glucose and fructose can be detected simultaneously in mixtures by UV-vis spectroscopy[4]. Extensive mechanistic studies will be presented.

Another molecule of interest is sialic acid, an important cell surface residue and known biomarker for certain cancers. We detect sialic acid selectively[5] over a variety of commonly-interfering analytes *via* two different methods. The mechanism of complexation and signal transduction will be presented, including detailed NMR evidence.

Additional xanthene dyes we have used in our laboratory afford excellent fluorescence and colorimetric detection of amino acids such as cysteine and homocysteine. Homocysteine is under intense study as a biomarker for Alzheimer's and cardiovascular diseases. Cysteine[6] or homocysteine[6,7] can be detected selectively in the presence of each other. Other amino acids and related molecules tested to date do not interfere significantly. The electron transfer mechanism leading to homocysteine signal transduction is biomimetic and related to its relatively strong reducing properties[7].

We aknowledge the generous support of the National Institutes of Health (R01 EB002044).

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SYNTHESIS AND CHARACTERIZATION OF TETRAPYRROLIC LIGANDS: APPLICATIONS IN CATALYSIS AND MOLECULAR RECOGNITION

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For decades, chemistry of tetrapyrrolic macrocycles mainly concerned the preparation and the study of porphyrins. Undoubtedly, this has to be correlated to an acceptable synthetic availability, and a rich coordination chemistry. More recently, oligopyrrolic macrocycles underwent a renewed interest with the discovery of reactions that allowed the preparation of macrocycles hardly available in the past. Thus, long known macrocycles like corroles or calixpyrroles are now commonly reported and their coordinating and catalytic properties thoroughly examined.

In this context, our group devoted much effort into synthesizing and studying porphyrins, corroles[1] but also calixphyrins and other macrocycles developed for applications in molecular recognition. Our most recent results concerning the enantioselective catalysis will be presented. In particular, we will underline the results we obtained in the enantioselective epoxidation of styrene derivatives using binap-porphyrin catalysts[2,3]. We will also describe the preparation of functionalized calix[4]phyrins and their use for anion sensing. Special emphasis will be dedicated to an unprecedented chiral binap-calixphyrin dimers (Fig. 1)[4]. At last, we will also introduce our recent results concerning the synthesis of dipyrrolylquinoxaline-including tetrapyrrolic macrocycles[5,6].

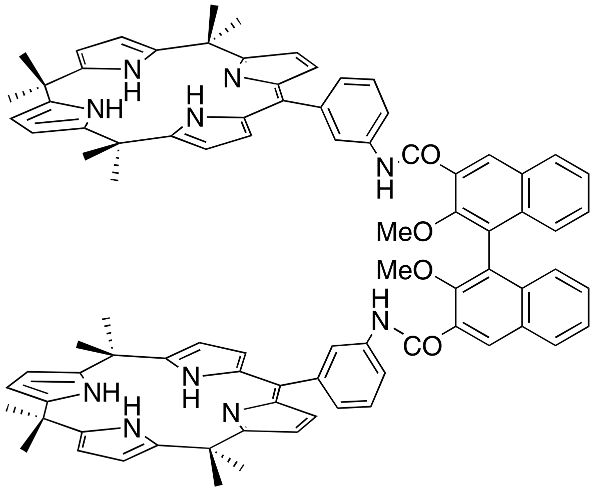

Fig. 1.

B.A. and E.R. thank the CNRS for financial support. MB acknowledges the French Embassy in Prague for financial support.

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SUPRAMOLECULAR CYLINDERS THAT RECOGNISE THE DNA MAJOR GROOVE AND INDUCE DRAMATIC INTRAMOLECULAR DNA COILING

L.J. CHILDS, J. MALINA, J.M.C.A. KERCKHOFFS, A. RODGER and M.J. HANNON*

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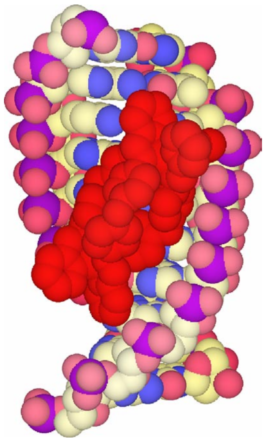

NMR structure of a cylinder in the major groove of DNA

Within biological systems, sequence specific DNA recognition is achieved by the surface motifs of proteins, which generally interact non-covalently with the major groove of DNA. Such protein recognition of DNA contrasts with that of synthetic small molecule recognition agents. Being smaller in scale than proteins, they tend to target the minor groove or act via intercalation.

We have pioneered the use of supramolecular chemistry to design agents which are of similar size and shape to natural biomolecule recognition units. In particular we have developed metallo-supramolecular cylinders which are a similar size and shape to the zinc finger motifs found in certain DNA-recognition proteins.

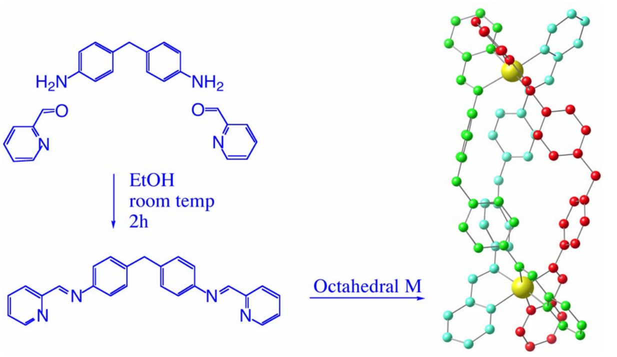

Fig. 1. Preparation of a supramolecular cylinder

These tetracationic supramolecular cylinders are ~2 nm in length and ~1 nm in diameter and assembled through metal-ligand interactions in one-pot mixing reactions of commercial aldehydes, amines and metal salts. The cylinders are tetracationic and contain three molecular strands wrapped around two iron(II) metal centres in a triple-helical fashion. They are chiral and exists in two enantiomeric forms.

We have demonstrated that these synthetic tetracationic supramolecular cylinders bind strongly (binding constant > 10^7 M^{-1}) and non-covalently to DNA in the major groove (as zinc fingers do) and induce dramatic and unexpected intra-molecular DNA coiling that is unprecedented with synthetic agents and somewhat reminiscent of the effect of histones. AFM images suggest that it the coiling is a cooperative process that starts at one end of the DNA.

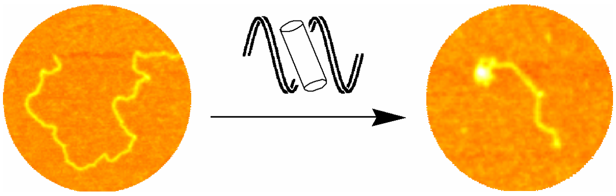

Fig. 2. AFM images of the cylinder coiling DNA

The remarkable structural effects that we have seen arise in large part from steping up in size the synthetic molecule towards that employed in nature. The work has been further extended to design cylinders that act as DNA cleavage agents..

We thank the European Union and the Leverhulme Trust for funding. MJH is the Royal Society of Chemistry Sir Edward Frankland Fellow 2004-5

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PORPHYRINE RECEPTOR CONTAINING GLYCOSYLATED STEROID AND ITS SYNTHESIS

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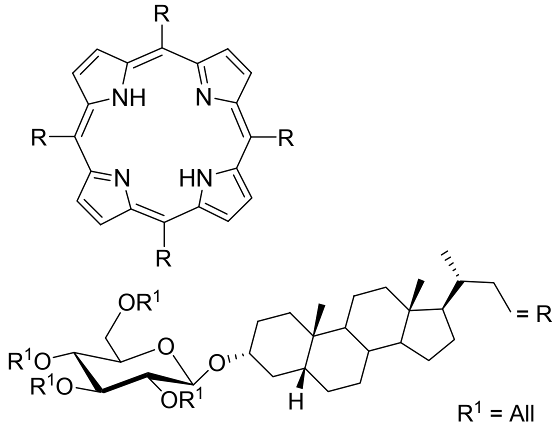
The suitable synthetic pathway for the new type of meso-substituted porphyrin (***X***) enables the study of this new kind of supramolecules and supramolecular synthons. These are being utilized in electrochemistry[1], membrane super assembly and biological studies, i.a. This work shows the preparation of a new complex type of conjugate and opens rather vast territory of their possible exploitations. The authors aimed to demonstrate the possibility of combining the known receptor molecules with carbohydrates that can serve as anchors, chiral selectors, or polarity modifiers, depending on their level and kind of protection. The receptor was based on glycosylated steroid-porphyrines[2] that can have many interesting properties. In recent works, porphyrine structures substituted in *meso* positions by steroid units with some interesting properties were prepared[3,4].



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Work was supported by projects of the Ministry of Education, Youth and Sports of the Czech Republic 1131 00001 and COST OC D31.

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SIMPLE SYNTHESIS OF *meso-C*-"GLYCOSYLATED" PORPHYRINS

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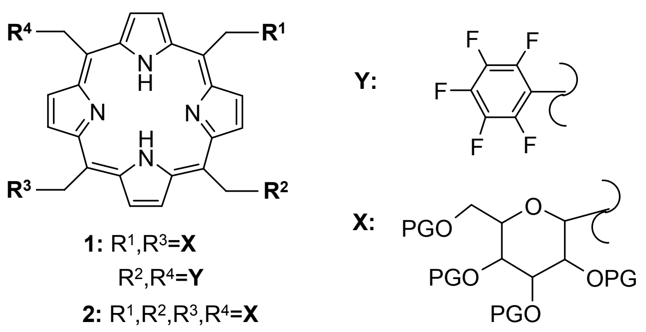
Compounds, where the active chromophore is conjugated with a vector on the basis of peptide, oligonucleotide, or saccharide[1] segment are of a great interest. Utilization of a chiral hyrdoxylated vector, here derived from a carbohydrate structure, predestinates this supramolecular synthon as the tool for molecular recognition in polar (aqueous, biological, i.a.) media[2-3]. Similar compounds were tested as sensitizers for photodynamic therapy and their interaction with DNA and nucleotides[4].

Aim of this project is a construction of porphyrin-saccharide conjugate, where the “sugar“ moiety is linked to the macrocycle in a *meso* position with a robust covalent C-C bonding, which, in difference from the *O*-glycosidic bond shows stability towards hydrolytic, or enzymatic degradation.

Synthetic part of this project developed several attempts to the *meso*-*C*-“glycosylated” porphyrins. Two basic strategies were used, one yielding the oligopyrrole heterocycle of the type **1** was based on sequential construction from the bipyrrole precursors; whereas the second, yielding to the porphyrine type **2** utilizes direct cyclisation of “sugar” aldehydes with pyrrole. Series of novel type compounds was fully characterized and is being studied on their properties and potential utilisation.



This work was supported by the Ministry of Education, Youth and Sports of the Czech Republic, with projects No. 2233 00006 (LK), OC D 31 (PD), and was a part of project Z4 055 905 (PS).

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DENDRITIC STEROID SYNTHONS

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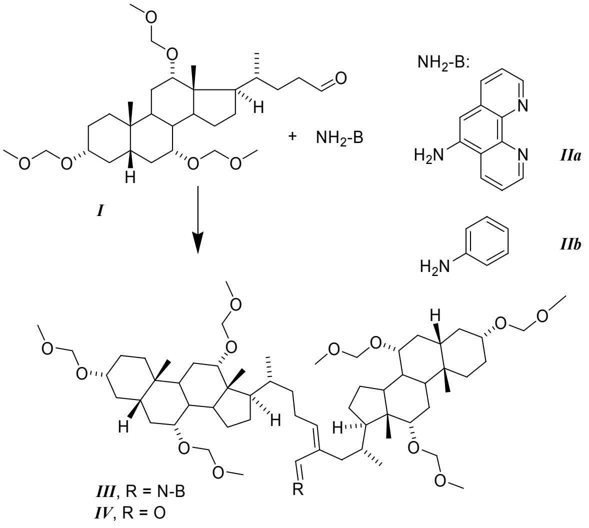
The quest for modified receptors and self-assembly blocks[1,2] yielded into the synthesis of several condensation products[3] resulting from the steroid side chain terminal aldehyde auto-condensation, induced by basic catalysis[4,5]. The influence of different bases was studied, i.a.

Firstly, there was aimed a simple Schiff base condensation product between bile acids and aromatic amines, however, the simple one was never detected. Contrary to the expectations, a new product type ***III*** was isolated. It represents dendritic synthon, which opens a way towards more complex steroidal structures with expected interesting properties.



Thus, 3α,7α,12α-tri(methoxymethoxy)-5β-cholan-24-al (***I*** refs[6,7]) was, upon basic catalysis condensed to branched dimeric condensation product with terminal aldehyde, which was further condensed without isolation with 5-amino-1,10-phenanthroline (***IIa***) in benzene. This reaction was compared with reactions of some other amines, and with aniline, similar condensation product was formed, whereas with pyridine and 1,10-phenanthroline there was no such condensation observed.

Aldehyde condensation is catalysed by the basic catalyst of the amine type. We suppose that amine must be involved in the first step of the reaction as a condensation reactant as the differences of the basicity of all four bases does not represent major reason for the reaction. Due to good prediction values of the ACD/Labs pK_a DB software[8] we list, besides the values found in the literature also the calculated pK_a values for corresponding phenanthrolines (see Table I).

Table I. Basicity of amines

	calculated[8] pK_a	literature pK_a
aniline	4.61	4.69 (20 °C)[9]
5-amino-1,10-phenanthroline	5.87	n/a
1,10-phenanthroline	4.86	n/a
pyridine	5.23	5.28 (20 °C)[10]

The above mechanistic construction is supported indirectly also by the fact, we were not able to isolate dimeric aldehyde ***IV***.

Since Emerson, Hess and Uhle demonstrated[11] that aliphatic Schiff bases can undergo aldol condensations and the pioneering aldol reaction on steroids was described on steroids[12] there were not much progress in utilization[13] of this approach for construction of branched chain or dendritic steroid structures. This communication, however, aims to show this possibility, mainly in connection of recent progress of the synthesis of steroid containing chiral multitopic catalysts[14].

The support from the research project Z4 055 905 (LD, IC, VP), from the Ministry of education of the CR, project No. 223300006 (PD) COST D-31 (MD) is greatly acknowledged.

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DIFFERENTIAL SENSING TECHNIQUES

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The use of synthetic and designed receptors for the analysis of complex analytes in real-life settings will be presented. Analytes in wine, blood, saliva, and chemical reactions, have been targeted using a protocol termed indicator-displacement[1]. The receptors derive from a combination of rational chemical design and modeling, with combinatorial synthesis techniques. Signaling is achieved by modulation of the absorbance and emission properties of indicators. The thermodynamics of the displacement assays will be discussed in detail, showing how threshold detection can be achieved. Further, it will be shown that a union of designed receptors targeted to a class of analytes with combinatorial synthesis gives patterns that differentiate between the individual members of the analyte class. The strategy is to use a core element that imparts a bias to each and every member of the library, ensuring affinity of the library members for the class of analytes being targeted. The design of this core derives from standard molecular recognition principles: preorganization, complementary, pair-wise interactions between receptor and analyte, and desolvation. Combinatorial techniques impart differential behavior and cross-reactivity, as is desired in an array sensing application[2]. The technique represents a marriage of supramolecular chemistry and pattern recognition protocols.

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EPOXIDATION OF TERMINAL OLEFINS WITH CHIRAL BINAPHTHYL PORPHYRINS

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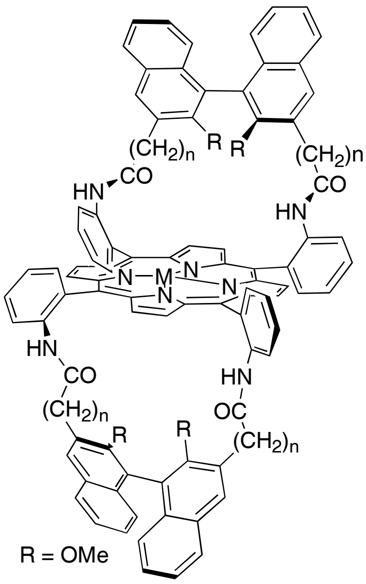
Studies using ironporphyrins as oxygenating catalysts were stimulated by the attempts to model the activity of cytochrome P-450 heme enzymes. The rigid macrocyclic core of porphyrins makes them attractive templates for building asymmetric catalysts. Different catalysts, with a $C2$ symmetry, have been prepared, showing impressive high ee and turnover numbers for asymmetric epoxidation of olefins with PhIO.



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INTERACTION OF PORPHYRINOID SENSITIZERS WITH NUCLEIC ACIDS

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Cationic porphyrinoid sensitizers have attracted considerable attention due to their binding affinity to nucleic acids, their ability to selectively cleave DNA, to inhibit human telomerases, and serve as vehicles for oligonucleotide delivery to tumors. Aggregation of porphyrins in an aqueous solution both with and without the presence of multipoint templates such as nucleic acids has an enormous impact on the ability of the sensitizers to generate singlet oxygen and to cleave nucleic acids. The properties of tetracationic porphyrins have been studied in detail[1,2], while little consideration has been devoted to porphyrins bearing two or three cationic substituents[3].

We report the properties of texaphyrins and peripherally substituted tetratolylporphyrins with two, three or four cationic groups including aggregation, photophysical properties and complexation with DNA. The monomeric porphyrins display similar photophysical properties, however, with considerable differences in self-aggregation and complexation towards DNA. The aggregation behavior, binding to DNA and photophysical properties of the sensitizers were studied using UV-vis and transient spectroscopy, resonance light scattering, circular dichroism and time-resolved luminescence of singlet oxygen.

Here we show that the number of charged peripheral substituents effectively controls hydrophobic/electrostatic forces and the nature of porphyrin aggregates and porphyrin-DNA forms. Nucleic acids with negatively charged phosphate groups shield repulsion forces between the porphyrin units that spontaneously assemble into helical assemblies deposited on the DNA surface. The helicity of the DNA backbone is imparted to the porphyrin assembly, resulting in induced chirality. Nucleic acids also facilitate the formation of J-aggregates. The lifetimes of the triplet states of monomeric sensitizers increase after binding, however, it does not prevent the formation of $^1O_2$.

This research was supported by the Grant Agency of the Czech Republic (Grant No. 203/02/0420 and 203/04/0426).

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PHOTOPHYSICAL PROPERTIES OF CYCLODEXTRIN-PORPHYRIN HOST-GUEST COMPLEXES

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Cyclodextrins (CDs) represent a class of macrocyclic host compounds having internal cavities capable of encapsulation of small molecules. Porphyrin sensitizers are too large to be completely encapsulated in the inner cavity. Instead, host-guest complexes can be formed incorporating a part of the sensitizer (*e.g.* phenyls of *meso*-substituted tetraphenylporphyrins) with the rest of the porphyrin molecule protruding to the bulk[1,2].

We report photophysical properties of anionic *meso*-tetraphenylporphyrins and cationic 5,10,15,20-tetrakis(*N*-methylpyridinium-4-yl)porphyrin bound to CDs. It is evident that binding of porphyrins is sensitive to the nature and size of their peripheral substituents, preferentially incorporated into the cavity. The binding constants depend strongly on the cavity size and functionalization of CDs and are in the range of 10^3 to 10^5 M^{-1}. The binding modes of *meso*-tetraphenyl substituted porphyrins can be classified into three types: i) Inclusion through the secondary face of CDs. ii) Inclusion through the primary face. iii) Non-specific external binding. The mode comprises direct contacts between the CDs exterior and porphyrin monomer or aggregate and is the least noteworthy for carrying sensitizers.

The noncovalent interaction between CDs and anionic tetraphenylporphyrin sensitizers affects their spectral and photophysical properties such as a bathochromic shift of the Soret band and the lifetimes of the triplet states in the absence or presence of oxygen. Because of the shielding effect of CDs, the bound sensitizers are protected from aggregation and binding to other components in a solution. The inclusion of the porphyrins in the cavity of CDs has a minor effect on their photophysical properties, *i.e.* the quantum yields of fluorescence, of the triplet states and of the singlet oxygen formation. In general, the singlet oxygen producing anionic tetraphenylporphyrins do not loose their sensitizing properties after binding to CDs.

This research was supported by the Grant Agency of the Czech Republic (Grant No. 203/02/0420 and 203/02/1483).

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SIMULTANEOUS FORMATION OF INCLUSION COMPOUND AND NICKEL NANOPARTICLES

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We develop a new simple method to obtain nickel nanoparticles. The synthesis carried out mixing bis(1,5 cyclooctadiene)-nickel(0) in THF and thiourea in methanol solutions. Transmission electron microscopy (TEM), X-ray Photoelectron Spectroscopy (XPS) and powder X-ray diffraction (XRD) were used for the characterization of nickel nanoparticles in colloidal solution. TEM images showed uniformity of particles size (50±10 nm), Electron-Diffraction pattern (ED) confirmed the metal natures of the resultant particles, besides XRD analysis of the white precipitate showed peaks corresponding to the phase of cyclooctadiene-thiourea inclusion compound.

Projects FONDECYT 1010891, 1040581. Deutscher Akademischern Austauschdienst/ DAAD.

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IMPROVED WETTING COMPATIBILITY OF NANOCRYSTALLINE PbSe ON Si(100) BY SAM SURFACE MODIFICATION

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Chemical bath deposition from solution offers a simple and cost-effective route for the fabrication of high quality semiconductor thin films, and is particularly advantageous for the synthesis of nanocrystalline semiconductors, in which the energy bandgap, E_g, can be adjusted by controlling the grain size of the films due to the quantum size effect. Lead selenide (PbSe) semiconductor films are used in IR detector applications, as well as for other photonic applications. This work presents the microstructure and morphology evolution in nanocrystalline PbSe films chemically deposited on GaAs(100), GaAs(111) and Si(100) substrates. High quality films were obtained on GaAs, while discontinuous islands were obtained on Si(100) at all deposition conditions. We suggested that the wetting properties of these materials can be improved by depositing self-assembled organic monolayers (SAM) prior to PbSe deposition. Organochlorosilane molecules with thiol terminated tails were chosen so that the silane group created strong covalent bond with the oxygen in silicon oxide layer of the substrate while SH group strongly interacts with the lead cations in solution. Preliminary results showed near continuous PbSe films even at short deposition times and low temperatures, in contrast to films that were obtained under the same conditions on untreated Si substrates, that showed PbSe islands sparsely distributed on the Si(100) surface.

CATALYTIC REDUCTION OF HALO – ALKANES IN AQUEOUS SOLUTIONS BY Ni(I) – TETRAAZA MACROCYCLIC COMPLEXES. A KINETIC AND AN ELECTROCHEMICAL STUDY

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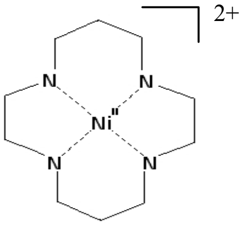
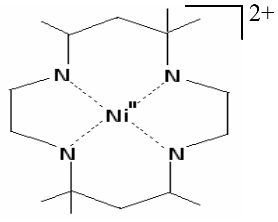
There is a major interest in the dehalogenation of halo-organic compounds due to their role as pollutants.

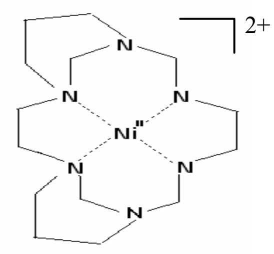
This study is about the catalytic dehalogenation of bromoacetic acid and chloroacetic acid in aqueous solutions. In the presence of $Ni(I)L^1$ produced radiolytically at alkaline pHs, bromoacetic acid is dehalogenated with a turnover of ~ 48 ($G(Br^-) = 288$) while chloroacetic acid is dehalogenated with a turnover of ~ 9.3 ($G(Cl^-) = 56$) in the case of $Ni(I)L^1$



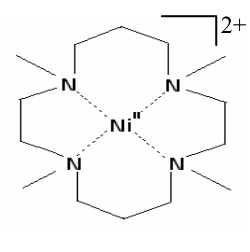
L¹



L² (meso)



L³



L⁴ (trans I)

The efficiency of the complex depends on the redox potential of the central cation.

All the complexes studied were proved to be good electrocatalysts for the reduction of the halogenated substrates. The mechanistic implications of the reduction processes are discussed.

MOLECULAR RECOGNITION OF ORGANIC SPECIES BY POLYFUNCTIONALISED HEXAAZAMACROCYCLES

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Hexaazamacrocycles are versatile molecular receptors. They are capable of forming molecular complexes with weak acids, such as phenols and their derivatives, and also carboxylic acids. Molecular recognition of phenol derivatives by lipophilic hexazamacrocycles has been investigated by means of Langmuir technique, and will be reported in this contribution

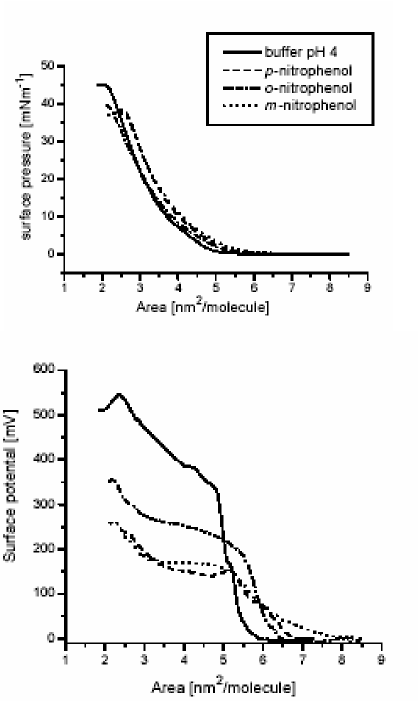

Fig. 1. Surface pressure and surface potential isotherms of ligand **1**.

Organic acids are important compounds in commerce, pharmaceutics, biochemistry and the environment.

We present the synthesis of 2,6-diaminopyridine derivatives of hexaazamacrocycle (**2**, **3**) and their properties as receptors for organic acids.

The hexaazamacrocycle receptors can interact at low pH with guests through amino cavity and also through hydrogen bonds between nitrogen atoms of 2,6-diaminopyridine and carboxylic groups of organic acids. These compounds have been used as sensitive sensors for flow-analysis of carboxylic acids.

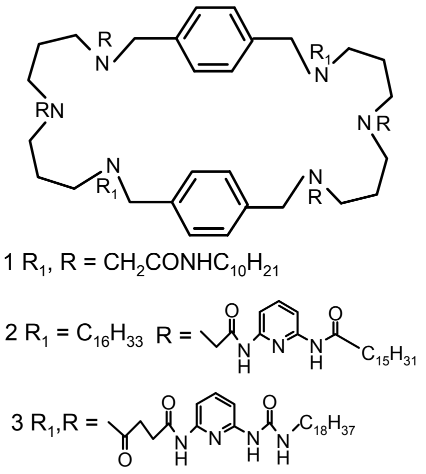

Fig. 2. Structures of investigated hexaazamacrocycles

CHIRAL SEPARATION: DESIGN OF ENANTIOSELECTIVE RECEPTORS BASED ON THE CHOLIC ACID STRUCTURAL BACKBONE

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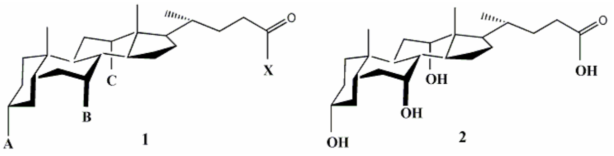
Enantioselective recognition is a long-standing issue in supramolecular chemistry with the preparation of enantiopure compounds for the pharmaceutical and chemical industries one of the major challenges facing chemists today. The design of enantioselective "synthetic receptors" that bind enantiomers and draw them across phase boundaries is one approach used. At anterio, a rational molecular modeling strategy is applied to the design of new host compounds: accurately relating computed binding free energies (BFEs) to existing experimental ee´s, new receptors are predicted on the basis of computation alone.



Scheme 1.

Receptor type architectures such as **1** derived from cholic acid **2** have particular advantages. The steroidal framework provides a chiral scaffold that positions codirected subunits (A, B, C) so as to create a binding site for a small-to-medium sized molecule. X can be used to control solubility.

Results obtained for receptors of type **1** and separation of *N*-acyl-α-amino acids, and Naproxen will be presented. Exhaustive conformational searches using a mixed mode Monte-Carlo (MCMM/LMCS) algorithm were followed by computation of BFEs using the MINTA[1] (mode integration) approach. MINTA was found to reproduce trends in experimental ee´s for a series of amino acid receptors once key MMFFs forcefield parameters involved in the binding were reparametrized.[2] In cases where the receptors tested were sterically very diverse, forcefield reparametrization was not required to obtain accurate predictions.

Work was supported in part by the European Union´s Human Potential Programme under contract HPRN-CT-2001-00182, "Chiral Receognition: Towards the Separation of Racemates".

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SEMICONDUCTOR NANOCRYSTALS ON POLYDIACETYLENE (PDA) LANGMUIR FILMS

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Lead sulfide (PbS) and silver sulfide (Ag_2S) semiconductor nanocrystals were prepared in ambient conditions by the exposure of crystalline polydiacetylene (PDA) Langmuir films to H_2S gas. The deposited nanocrystals were studied by transmission electron microscopy (TEM), ultrahigh resolution scanning electron microscopy (UHR-SEM), atomic force microscopy (AFM) and X-ray diffraction (XRD) analyses in order to investigate the morphology and orientation relationship existing between the nanocrystals and the PDA template.

Highly oriented arrays of PbS nanocrystals were obtained, with three distinct, coexisting nanocrystal orientations with typical shapes corresponding to each orientation. The $<110>_{PbS}$ direction was aligned parallel to the PDA linear direction for all orientations, indicating a template-directed growth for the PbS/PDA system. Control over the deposition was obtained by varying the $PbCl_2$ subphase concentration [1,2].

When the subphase solution was replaced with $AgNO_3$, two Ag_2S nanocrystal populations were obtained: small nanocrystals, ca. ***8*** nm in diameter arranged, that were along the PDA strands, and larger nanocrystals of ca. ***50*** nm that were formed in the voids between the PDA domains. The concentration of the Ag^+ ions in the subphase was shown to control the nanocrystal film morphology and surface coverage. The linearly arranged nanocrystals were not oriented with respect to the PDA film template [3]. Finally, the role of the metal cation valency (M^{x+}) in the deposition of M_xS nanocrystals on PDA Langmuir films is discussed..

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LIQUID-CRYSTALLINE LANTHANIDE COMPLEXES

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Lanthanide complexes with a disklike shape (discotic complexes) can form liquid-crystalline phases upon heating. In these liquid-crystalline phases or mesophases the molecular order is between that of an ordered solid and a disordered liquid. The mesophase is an anisotropic fluid. In columnar mesophases, the molecules are stacked into columns. Depending on the type of 2D lattice formed by the columns, one can make a distinction between a hexagonal columnar phase (Col_h), a tetragonal columnar phase (Col_t) or a rectangular columnar phase (Col_r). To stabilize the mesophase and to reduce the transition temperatures, long alkyl chain are attached to the disklike core of these complexes. At the melting point, the alkyl chains obtain a disordered liquid-like conformation, but the columns remain intact. At the clearing point (second melting point), the columnar supramolecular organization is lost. A powerful experimental tool to study these complexes is high-temperature X-ray diffraction, but also hot-stage polarizing optical microscopy (POM) and differential scanning calorimetry (DSC) can provide valuable information.

In this presentation, an overview of different types of discotic liquid-crystalline lanthanide complexes will be given [1]. Special attention will be paid to the substituted bis(phthalocyaninato)lanthanide(III) complexes in which the lanthanide ion is sandwiched between two phthalocyanine rings[2]. The lutetium compounds can be considered as one-dimensional molecular semiconductors, and most of these complexes show electrochromism. Another type of interesting compounds is the class of metal-containing liquid crystals (metallomesogens) that contain both a lanthanide ion and a transition metal ion. Different types of liquid-crystalline f-d complexes will be discussed[3], as well as compounds derived from substituted 1,10-phenanthrolines.

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SUBSTITUENT EFFECTS IN THE BINDING OF BIS(4-FLUOROBENZYL)AMMONIUM IONS BY DIANILINO[24]CROWN-8

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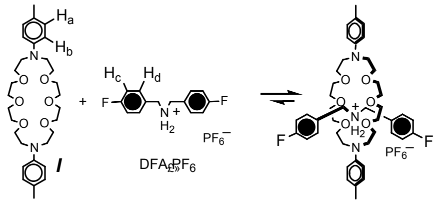
We have synthesized a series of para-substituted dianilino[24]crown-8 (DA24C8) macrocycles and investigated their ability to form host–guest complexes with bis(4-fluorobenzyl)ammonium ions (DFA^+). Although these crown ethers contain weakly hydrogen bonding aniline motifs, they do bind DFA^+ in $CDCl_3/CD_3NO_2$ solution, presumably in a pseudorotaxane-like manner[1]. A plot of the values of the relative binding strengths ($\log[K_a(R)/K_a(H)]$) versus the Hammett substituent constants σ^+ of the groups at the para-position of the aniline units suggests that a linear free energy correlation exists for this self-assembly process[2]. The strength of the binding between the crown ether and the thread-like ion can be fine-tuned over a narrow range by judicious choice of the substituting groups.



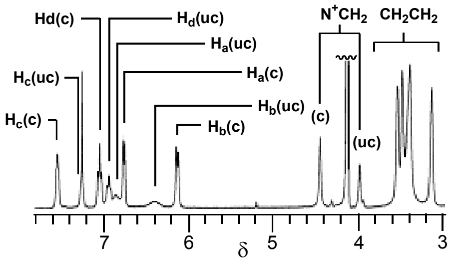


Fig. 1. Partial ^1H NMR spectrum [400 MHz, $CDCl_3/CD_3NO_2$ (2:1), 223 K] of an equimolar mixture (20 mM) of ***I*** and $DFA{\cdot}PF_6$, which demonstrates that uncomplexed (**uc**) and complexed (**c**) species equilibrate with one another slowly on this NMR spectroscopy timescale.

We thank National Science Council for financial support (NSC 91-2113-M-002-055).

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ORGANISING NON-COVALENT CHEMICAL SYSTEMS WITH SELECTED FUNCTIONS

Presentation of COST D-31 project

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The main objective of the COST Action D-31 is to develop the knowledge in the extremely promising area of supramolecular synthesis, of organised and/or of self-organised chemical systems in order to master organisational complexity starting from simplicity. This Action is not only concerned with synthetic and structural aspects of supramolecular organisations, but aims at the design, preparation, and optimisation of functional chemical systems[1].

Among the selected themes to deal with it could be pointed out i.a.: High Yield Synthesis by Template Effects; Structural Methodology for Functional Molecular Organised Systems; Tectonics; Molecular Organisations on Surface and Confined Space, Selective orientation of the systems, Modified properties of the system due to surface interaction, Surface assisted assembly of systems, Patterned assembly on prepared surfaces, Generation of directional structures, Communication with systems, Low molecular weight organogelators, Control of mechanical bonding, Reactivity as Selective Function, Generation of diversity, Dynamic and virtual libraries with functions, Receptor based functional architectures, Chirality generation and amplification through self-assembly, Conformational control of self-assembled structures by external stimuli, Biomimetic functional molecular assemblies, Channel formation through supramolecular organisation and self-assembly.

The general audience is invited to the Kickoff workshop (November 7-8, 2004)[2], as well as to submit Working Group Proposals[3], or just to join the action. The action is proposed for five years with effect from 27 February 2004, twenty countries signed up to August 2004.

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Author Index

Abraham, Yael s76
Adjimatera, Noppadon s22, s23, s24
Aguirre, Ángel s87
Ahn, Cheol-Hee s31
Aida, Takuzo s67, s89
Akasheh, Talal s20
Akkaya, Engin U. s60, s61
Al-Ani, Khalid Essa s20
Alaverdian, Yuriy S. s53
Albrecht, Markus s33, s47, s48
Alfimov, Michael V. s10, s11, s36
Alfimov, Michail V. s53
Alfonso, Ignacio s87, s89
Amari, Nadia s7
Andraud, Chantal s7
Andrioletti, Bruno s104, s108
Andronati, Sergey s6
Andryukhina, Elena N. s10, s11, s 36
Anisimov, Alexander V. s51
Anslyn, Eric V. s108
Appelhans, Dietmar s72
Araki, Koiti s18
Astafiev, Dmitriy A. s56
Atlas, G. s87
Aurell, M. José s77
Avlasevich, Yuri S. s10
Baer, Ingmar s93, s94
Baldeck, Patrice L. s7
Bañuls, M. José s77
Baralia, Gabriel G. s36
Barbu, Anca Elena s55
Bartoš, Petr s41, s59
Bassett, A. s82
Belman, Nataly s112
Bělohradský, Martin s70
Benaliouche, Fouad s5
Bergman, Robert G. s83
Bergmann, R. s35
Berman, Amir s112
Bernátková, Markéta s104
Bettelheim, A. s17, s87
Betti, Paolo s16
Bikádi, Zsolt s57
Binnemans, Koen s25, s26, s113
Biros, Shannon M. s58
Bittner, S. s103
Blafková, Petra s75
Blagbrough, Ian S. s22, s23, s24
Bobylyova, Alla A. s51
Bogucki, Andrzej s34
Boguta, Andrzej s10
Bomkamp, Martin s53, s54
Borczyskowski (von), Christian s22
Botbol, Silvina s110
Boucheffa, Youcef s5
Březnová, Hana s73
Brinker, Udo H. s27, s50
Brisset, Hugues s25
Broncová, Gabriela s65, s73, s74
Bucharov, Sergei V. s93
Bucher, Christophe s95
Buděšínský, Miloš s66, s68
Bunzen, Jens s45
Bünzli, Jean-Claude G. s92
Burilov, Alexander R. s93, s94
Buschmann, Hans-Jürgen s55
Caltagirone, Claudia s39
Cantadori, Barbara s16
Caradoc-Davies, Paula L. s37
Cardinaels, Thomas s113
Caskey, Douglas C. s69
Castano-Briones, M. M. s82
Černý, Ivan s107
Chaix, Carole s25
Chan, Yi-Tsu s42
Chauvin, Anne-Sophie s92
Chen, Chao-Tsen s28
Chen, Chin-Ti s14
Chen, Dong-Hwang s19
Chen, Jwu-Ting s58
Chen, Y.-C. s58
Cherif, Mohamed Fodil s5
Childs, L.J. s105
Chiu, Sheng-Hsien s113
Cho, Dong-Gyu s95
Cho, Won-Seob s95
Choi, Jeongsoo s30, s60
Choi, Yi-Rac s31
Chun, Se Kyeong s60
Chung, Jae Woo s29
Churakov, Andrei V. s43
Churakov, Andrei s21
Cígler, Petr s94, s95
Císařová, Ivana s64, s68, s70
Cohen, Haim s11, s34, s111
Constable, Edwin C. s19
Constantinescu, Titus s55
Costero, Ana M. s70, s77
Csöregh, Ingeborg s15
Czerwenka, Christoph s5
Dabirian, Reza s35
Dalcanale, Enrico s16
De Cola, L. s81
Dehaen, Wim s103
Depraetere, Stefaan s103
Dequiang, An s95
Dias, Sandra s33
Djedovic, Natasha K. s85
Dolenský, Bohumil s97
Donnio, Bertrand s113
Dotsenko, Ivan P. s56
Drašar, Lukáš s107
Drašar, Pavel s106, s107, s114
Dukh, Mykhaylo s107
Eichen, Yoav s76
Elliott, Elizabeth s85

Enikeev, Konstantin M. s93
Escobedo, Jorge O. s103
Fages, Frederic s13, s25
Faiz, J. s81
Fan, Sheng-Di s90
Fedorov, Yuri V. s10, s11, s36
Fedorova, Olga A. s10, s11, s36, s51, s53
Feofanov, Alexei V. s17, s53
Ferdani, Riccardo s85
Fias, Pascal s26
Fiedler, Dorothea s83
Fitos, Ilona s57
Fomine, Serguei s86
Fowler, Chris s95
Fröhlich, Roland s33, s47, s48
Fuji, Kaoru s12
Fukushima, Takanori s89
Furuta, Hiroyuki s30, s98
Fyfe, Colin A. s28
Gale, Philip A. s77, s95
Galow, Trent H. s81
Garau, Alessandra s39
García Granda, Santiago s87
Gaviña, Pablo s90
Gazizov, Almir S. s94
Ghorbani, Mohammad s9
Gil, Agnieszka s111
Glover, P. B. s82
Gokel, George W. s85
Golan, Yuval s110, s112
Gomes, José A. N. F. s37
Gomes, José R. B. s76
González-Álvarez, Almudena s87
Gorbatchuk, Valery V. s32
Görller-Walrand, Christiane s25
Gotor, Vicente s87, s89
Graja, Andrzej s34
Grimme, Stefan s54
Grin, Michael A. s17
Grinberg, S. s103
Gromov, Sergey P. s53
Gross, Dustin s95
Gross, Zeev s101
Guadarrama, Patricia s86
Gubin, Sergey P. s56
Guillon, Daniel s113
Guo, Yan-Ming s67
Gutakovsky, Anton K. s34
Habicher, Wolf D. s93, s94
Haider, J. M. s81
Haj_Zaroubi, Manal s101
Hannon, M. J. s105
Hanton, Lyall R. s37
Hapke, Marko s45, 47
Hashizume, Mineo s88
Hashizume, Tomihiro s89
Hass, Oliver s46
Havel, Josef s8, s40
Haworth, Ian S. s23
Hayes, Joseph M. s112
Heil, Martin s44
Heinze, Susanne s46
Heirtzler, Fenton s33
Herdtweck, Eberhardt s97
Hermann, Petr s8, s40
Hill, Jonathan P. s89
Hirao, Toshikazu s62
Hirota, Shun s71
Hlávka, Karel s66
Hnatejko, Zbigniew s20, s40
Hodačová, Jana s66, s68, s102
Hof, Fraser s58
Hof, Martin s22, s79
Holý, Petr s64, s70
Horinek, Dominik s69
Houjou, Hirohiko s48
Housecroft, Catherine E. s19
Howard, Judith A. K. s43
Howard, Judith s21
Huang, Chien-Huang s28
Hub, Martin s74, s75
Ichihara, Hideki s89
Ikeda, Atsushi s88
Inoue, K. s35
Irajizad, Azam s9
Ishii, Noriyuki s89
Itahara, Toshio s48, s49
Ito, Kohzo s89
Iwamoto, Yoshifumi s49
Jadhav, Vinod D. s101
Janser, Ingo s33, s48
Janssen, Dimitri s103
Jara, Paul s110
Jedliński, Zbigniew s64
Jelínek, L. s35
Jenneskens, Leonardus W. s35
Jeon, Jae-Deok s28
Jin, Wusong s89
Jonas, Alain M. s36
Juranović Cindrić, Iva s38
Juzwa, Maria s63
Kamikado, Toshiya s15
Kanda, Junpei s48
Kano, Koji s71
Kapon, Moshe s76
Karmakova, Tatyana A. s17
Kassies, Roel s17
Kasymova, Elmira M. s93
Kawabata, Takeo s12
Kerckhoffs, J. M. C. A. s105
Khoroshutin, Andrey V. s51
Kiehne, Ulf s45
Kikuchi, Jun-Ichi s88, s90
Kim, Chulhee s92
Kim, Keon-Hyeong s31
Kim, Sung Ho s60
Kirchner, Ralf s72
Kitagawa, Susumu s67

Kitagishi, Hiroaki s71
Kłonkowski, Andrzej M. s20
Kniežo, Ladislav s106
Knyazeva, Irina R. s94
Kodera, Masahito s71
Koivukorpi, Juha s42
Kolehmainen, Erkki s42
Komber, Hartmut s72
Konovalov, Alexander I. s93, s94
Konvalinka, Jan s95
Korin, E. s87
Korobov, Maxim S. s56
Korovin, Yuriy s6
Kosaka, Atsuko s89
Koščová, Simona s68
Kost, Svetlana s6
Kotani, Haruo s88
Kotek, Jan s8
Kottas, Gregg S. s69
Kováč, Martin s64
Kozáková, Michala s66
Kral, Teresa s22
Král, Vladimír s42, s61, s65, s66, s73, s74, s75, s91, s94, s95, s96, s97, s98, s101, s104, s107, s109
Králová, Jarmila s75, s94
Krondak, Martin s65, s66
Kubát, Pavel s109
Kukal, Jaromír s65
Kulikov, Oleg s6
Kuś, Piotr s17
Kusumoto, Tomokazu s11
Kuz'mina, Lyudmila G. s43
Kuz'mina, Lyudmila s21
Kwak, Seung-Yeop s28, s29, s30, s60
Lah, Jurij s8
Lahtinen, Manu s16
Lang, Kamil s109
Lange, S. s35
Langner, Marek s22
Łapiński, Andrzej s34
Lavayen, Vladimir s110
Lee , Gene-Hsiang s56
Lee, Chung-Chou s56
Lee, Min-Hyung s31
Lee, Sang Wha s92
Leevy, W. Matthew s85
Lehn, Jean-Marie s43
Lemercier, Gilles s7
Leung, Dennis H. s83
Leusser, Dirk s14
Levitskaia, Tatiana G. s95
Li, Cong s80
Liao, Kang-Shyang s113
Liao, Min-Hung s19
Lin, Hong-Ping s42
Lin, Y.-C. s58
Lin, Yen-Chen s27
Lindner, Wolfgang s5
Lippolis, Vito s39
Lis, Stefan s20, s21, s40
Liu, Shiuh-Tzung s42
Lodewyckx, Katleen s113
Lohner, Karl s27
Lomadze, Nino s87
López-Ortiz, Fernando s87
Lubal, Přemysl s8, s40
Lukeš, Ivan s8, s40
Lützen, Arne s45, s46, s47
Maeda, Hiromitsu s30
Magalhães, Alexandre L. s37
Magda, Darren J. s95
Magnera, Thomas F. s69
Mahammed, Atif s101
Maimon, E. s17, s87
Maimon, Eric s34, s111
Malina, J. s105
Mandrand, Bernard s25
Marhol, Petr s96
Marquez, Manuel s95
Marten, J. s39
Martineau, Cécile s7
Mashiko, Shinro s15
Mashura, Marina M. s36
Matějíček, Pavel s95
Matějka, Pavel s65
Matějka, Z. s35
Maurizot, Jean-Claude s17
Mazal, Ctibor s41, s59
Meić, Zlatko s38
Mel'nikov, Sergey M. s27
Merchán, Juan s110
Merkas, Sonja s84
Meyerstein, Dan s11, s34, s111
Michele, Grassi s16
Michl, Josef s59, s69
Mieusset, Jean-Luc s50
Milekhin, Aleksandr G. s34
Mirk, Daniela s54
Mironov, Andrey F. s17
Mirsky, Vladimir M. s74
Mirsky, Vladimir s73
Miyaji, Hidekazu s95
Mizoguchi, Noriyuki s41
Mizutani, Tadashi s67
Mlinarić-Majerski, Kata s40
Moriuchi, Toshiyuki s62
Mosinger, Jiří s109
Mou, Chung-Yuan s42
Moustrou, Corinne s25
Moyer, Bruce s95
Mukmeneva, Natalia A. s93
Mulatier, Jean-Christophe s7
Mulcahy, Mary E. s69
Mustata, Roxana s101
Mutihac, Lucia s55
Nakatake, Shinichi s49
Nampally, Sreenivasachary s43
Nasirpouri, Farzad s9

Naumovski, Louie s95
Navarro, Aude-Emmanuelle s25
Neuberger, Markus s19
Nishikawa, Masaru s49
Nockemann, Peter s26
Nolting, Rainer s47
Noskova, Oxana s21
Nový, Jakub s50, s57
Nummelin, Sami s16
Nysten, Bernard s36
Obukhova, Natalya A. s52
Oike, Hideaki s67
Okuno, Yoshishige s15
Olejniczak, Iwona s34
Orlewska, Czeslawa s103
Osswald, Peter s14
Osuka, Atsuhiro s96
Otto, Cees s17
Pabst, Georg s27
Pacco, Antoine s25
Pajewska, Jolanta s85
Pajewski, Robert s85
Palivec, Lukáš s51
Palm, Barbara s87
Panfilov, Michael A. s10
Pankratov, Denis A. s56
Paolesse, Roberto s99
Park, Chiyoung s92
Parschová, H. s35
Pavlovsky, Victor s6
Peña–Gónzalez, Carmen s89
Peng, Shie-Ming s56
Pereira Silva, M. J. J. s81
Petrescu, Stefana M. s101
Piantanida, Ivo s13, s38
Pietraszkiewicz, Marek s111
Pietraszkiewicz, Oksana s111
Pikramenou, Z. s81, s82
Pirondini, Laura s16
Plešek, Jaromír s95
Pljutinskaya, Anna D. s17
Pospíšil, Lubomír s69
Poučková, Pavla s75, s94
Pouretedal, Hamid Reza s78, s79
Pourzand, Charareh s24
Pouzar, Vladimír s107
Pražáková, Martina s91
Příhodová, Jiřina s57
Prikhodchenko, Petr V. s43
Pudovik, Michail A. s93, s94
Puntus, Lada s92
Quelquejeu, Melanie s108
Radecka, Hanna s103
Radecki, Jerzy s103
Rakhmanov, Edward V. s51
Raston, Colin L. s19
Raymond, Kenneth N. s83
Raznoshik, Hava s34
Rebek, Jr., Julius s58
Refregiers, Matthieu s17
Ren, Qi-Zhi s108
Řezáčová¨, Pavlína s95
Řezanka, Pavel s73
Ribeiro da Silva, Manuel A. V. s76
Ribeiro da Silva, Maria D. M. C. s76
Richter, Asta s10
Rissanen, Kari s16, s114
Rodger, A. s105
Rodríguez, Saddys s110
Rodríguez-Muñiz, Gemma s90
Röllich, A. s35
Ropponen, Jarmo s16
Rose, Éric s104, 108
Rubinstein, A. s87
Rusakova, Natalya s6
Rusin, Oleksandr s103
Rybáček, Jiří s70
Rybáčková, Markéta s70
Ryu, Mi Kyo s92
Saedi, Amir Mehdi s9
Saeki, Naoko s67
Saki, Neslihan s61
Salman, Husein s76
Saltiel, Jack s10
Sanders, Jeremy K. M. s100
Sasaki, Yoshihiro s32
Sawatzki, A.-K. s35
Schepers, An s26
Schlesinger, Paul H. s85
Schmidtchen, Franz P. s65, s97, s101
Schmuck, Carsten s44
Schneider, Hans-Jörg s87
Schopohl, Matthias C. s54
Schubert, Ulrich s55
Schug, Kevin s5
Schutz, Osnat s11
Seichter, W. s39
Seichter, Wilhelm s15
Seidel, Jürgen s72
Semnani, Abolfazl s78, s79
Sessler, Jonathan L. s75, s95
Setnička, Vladimír s43, s61
Shames, A. I. s87
Shames, Alexander I. s17, s34
Shandalov, Lisa s111
Shandalov, Michael s110
Sharonov, George V. s17
Shen, Xiuliang s62
Shepel, Nikolay E. s36
Shimomura, Takeshi s89
Shriver, James s95
Shulga, Alexander s22
Siering, Carsten s54
Simonyi, Miklós s57
Škarka, Ondřej s59
Sleven, Jurgen s113
Smith, Christopher B. s19
Solladie, Nathalie s84

Song, Yumi s92
Speiser, Shammai s76
Spinelli, Nicolas s25
Staats, Holger s46
Stalke, Dietmar s14
Staninski, Krzysztof s21
Stein, Matthias s112
Štěpánek, Petr s106
Stephan, Holger s35
Strelko, Vladimir s26
Strongin, Robert M. s103
Su, Jen-Kuan s113
Suwattanamala, Akapong s37
Suwinska, Kinga s76
Sveshnikova, Larisa L. s34
Svobodová, Ivona s8, s40
Świetlik, Roman s10
Synytsya, Alla s75
Synytsya, Andriy s75
Szydlo, Florence s104
Táborský, Petr s40
Tamura, Hisashi s48
Tanima, Daisuke s12
Terashima, Takashi s88
Terekhova, Irina V. s52
Thiemann, Frank s46, s47
Tian, Wen-Jie s90
Tianjun, Liu s87
Tichý, Miloš s64
Tkadlecová, Marcela s51
Toma, Henrique E. s18
Trembleau, Laurent s58
Trnka, Tomáš s106
Try, Andrew s95
Tsai, Pei-Chang s14
Tsubaki, Kazunori s12
Tulyakova, Elena V. s51
Tumir, Lidija-Marija s38
Ueda, Takehiko s48, s49
Ullrich, Elke C. s58
Urbanová, Marie s43, s50, s51, s57, s61
Vagapova, Lylia I. s93
Valík, Martin s51, s65, s97, s98, s101
Van Deun, Rik s26
Van Hecke, Kristof s26
Van Meervelt, Luc s26
Vanwalree, Cornelis A. s35
Varbanov, Sabi s92
Vašek, Petr s94
Vasylyeva, Hanna s26
Veljković, Jelena s40
Venturi, Margherita s36
Vesnaver, Gorazd s8
Vigny, Paul s17
Voigt, Dieter s72
Voit, Brigitte s72
Volf, Radko s65, s66, s73, s74
Volka, Karel s43, s50, s51, s57, s61, s75
Volodina, Yulia M. s94
Vujasinović, Ines s40
Waldvogel, Siegfried R. s53, s54
Walla, Peter s27
Wang, Irène s7
Wang, Juen-Kai s14
Wang, Wie s85
Wang, Yu s27
Wang, Zhong s95
Wawruszak, Marie s94
Weber, E. s39
Weber, Edwin s15
Weber, Michelle s85
Weis, Patrick s33, s47
Weiser, Jörg s112
Wienand, Wolfgang s44
Williams, R. M. s81
Win, T. s103
Winnischofer, Herbert s18
Winter, Ingrid s27
Winter, Silke s15
Wolff, Oliver s54
Wong, Wing-Tak s80
Wróbel, Danuta s10
Wu, Kun-Yang s19
Würthner, Frank s14
Yakubovskaya, Raisa I. s17
Yamauchi, Takae s67
Yang, F.-Z. s58
Ydgar, R. s17, s87
Yeh, Hsiu-Chih s14
Yokoyama, Shiyoshi s15
Yokoyama, Takashi s15
You, Lei s85
Youseef, Yaser A. s20
Yu, Jenwei s14
Yukruk, Funda s60
Yurkov, Gleb Yu. s56
Yutronic, Nicolás s110
Záruba, Kamil s65, s73, s91
Závada, Jiří s64, s70
Zawidlak, Barbara s63
Zelenka, Karel s106
Zenkevich, Eduard s22
Zheng, Xiaolai s69
Ziganshin, Marat A. s32
Zilbermann, I. s17
Zilbermann, Israel s34, s87, s111
Žinić, Mladen s13, s38, s84
Zrig, Samia s104
Zsila, Ferenc s57