Book of Abstracts

SupraChem 2015

February 22 – 24, 2015

Freie Universität Berlin

Contents

General Information

Conference Location

Institut für Chemie und Biochemie der Freien Universität Berlin
Foyer und Hörsaal der Anorganischen Chemie
Fabeckstr. 34/36
14195 Berlin
Germany

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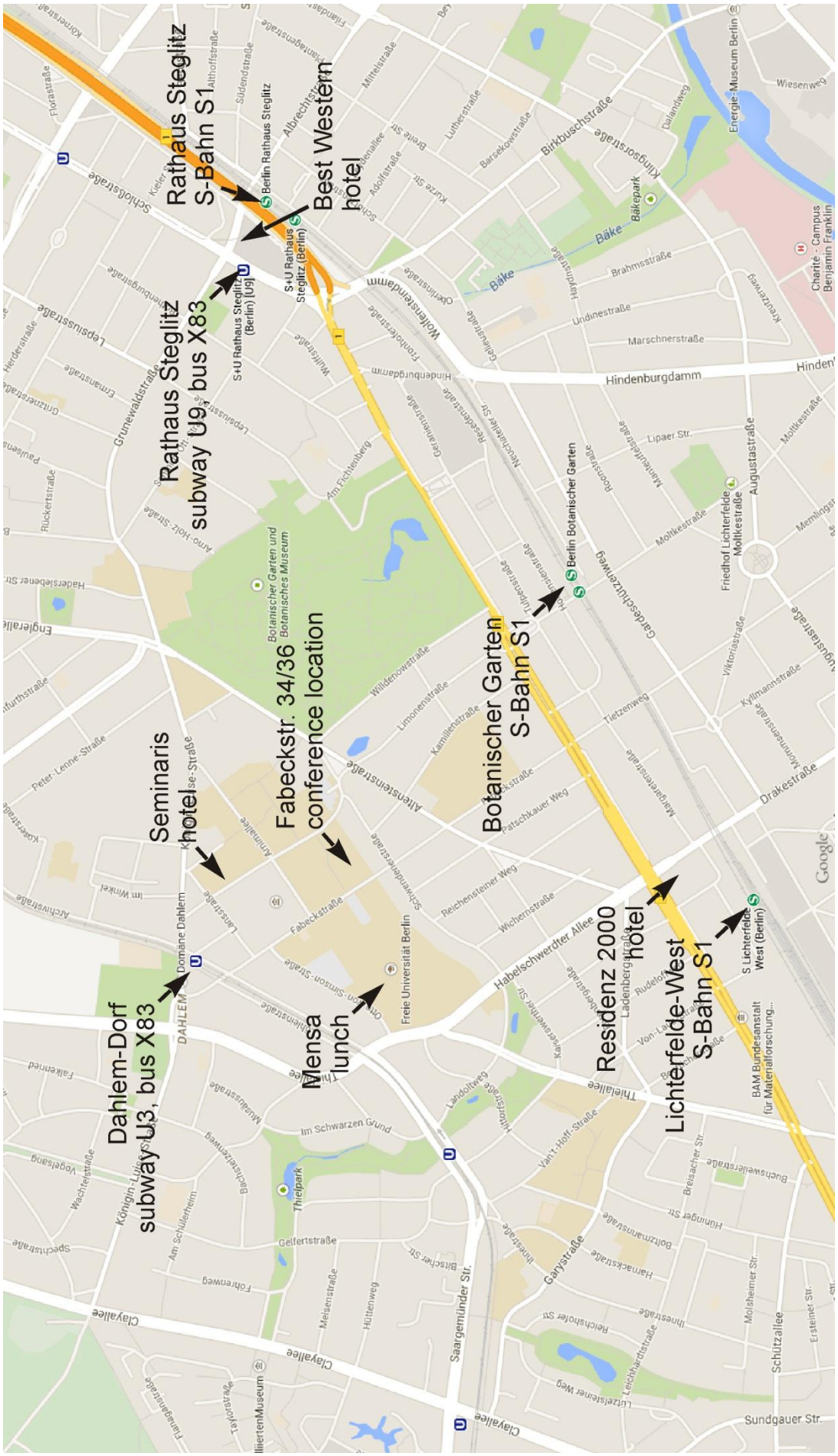
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Liebig-Vereinigung für Organische Chemie in der Gesellschaft Deutscher Chemiker

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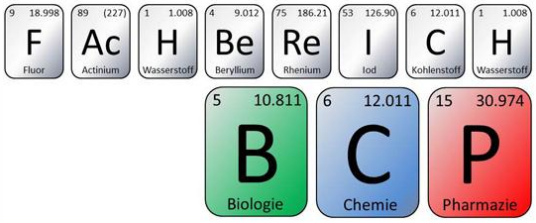

Fonds der Chemischen Industrie

Sonderforschungsbereich 765 "Multivalenz" der DFG

Professor Werdelmann-Stiftung im Deutschen Stiftungszentrum

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Program Schedule

Sunday, February 22, 2015

19:00-22:00 Informal Get-Together
Location: Fabeckstr. 34/36 (Inorganic Chemistry)

Monday, February 23, 2015, Morning Session

Metallosupramolecular & Subcomponent Self-Assembly

08:00-08:10 Welcome Remarks (Lützen/Schalley/Seiffert)

08:10-08:30 **Rahul Gera**, Tata Institute of Fundamental Research, Mumbai/IN
Optically triggering ultrafast bidirectional PCET inside a self-assembled Nanocage

08:30-08:50 **Guido H. Clever**, Georg-August-Universität Göttingen/D
Dynamics and Switching in Self-Assembled Hosts

08:50-09:10 **Astrid Schaly**, Université de Bourgogne, Dijon/F
Stereoselective Self-Assembly of Chiral Metallo-Organic Cryptophanes

09:10-09:30 **Markus Albrecht**, RWTH Aachen/D
"Remote control" of stereoselectivity in C-C forming reactions in the periphery of hierarchically assembled helicates

09:30-09:50 **Anna J. McConnell**, University of Cambridge, Cambridge/UK
Cobaltocene Mediated Reductive Coupling of Iminoboronates

09:50-10:10 **Michael Mastalerz**, Ruprecht-Karls-Universität, Heidelberg/D
Giant Boronic Ester Cages

Coffee Break

Capsules, Cages & Baskets

10:40-11:00 **Florian Beuerle**, Universität Würzburg, Würzburg/D
Shape-Controlled Synthesis and Self-Sorting of Covalent Organic Cage Compounds

11:00-11:20 **Konrad Tiefenbacher**, Technische Universität München, München/D
Enzyme-like catalysis in self-assembled aromatic cavities

11:20-11:40 **Jovica D. Badjic**, Ohio State University, Columbus/USA
The Selective Entrapment and Degradation of Nerve Agents with Amino-Acid Containing Baskets and their Assemblies in Water

11:40-12:50 *Keynote Lecture*
Jonathan R. Nitschke, University of Cambridge/UK
Transformative cages and luminous chains: functional materials through subcomponent self-assembly

Lunch Break

Monday, February 23, 2015, Afternoon Sesssion

Supramolecular Polymers

14:00-14:50 *Keynote Lecture*
Ulrich S. Schubert, Universität Jena, Jena/Germany
Metallo-supramolecular polymers

14:50-15:10 **Pol Besenius**, Westfälische Wilhelms-Universität, Münster/D
pH-Regulated Supramolecular Polymerisation

15:10-15:30 **Ievgen Donskyi**, Freie Universität Berlin, Berlin/D
Fullerene-Polyglycerol hybrids

15:30-15:50 **Soichiro Ogi**, Universität Würzburg, Würzburg/D
Seeded Supramolecular Polymerization of Perylene Bisimide Organogelator

Coffee Break

Anion Recognition

16:20-16:40 **Evgeny A. Kataev**, Technische Universität Chemnitz, Chemnitz/D
Recognition of phosphates by synthetic receptors

16:40-17:00 **Ivo Leito**, University of Tartu, Tartu/EST
Towards discrimination of carboxylates by hydrogen-bond donor anion receptors

17:00-17:20 **Werner M. Nau**, Jacobs-Universität, Bremen/D
The Chaotropic Effect: A Generic Driving Force for Anion Complexation

17:20-17:40 **Fabian Sommer**, Technische Universität Kaiserslautern, Kaiserslautern/D
Anion Binding by a Neutral Water Soluble Bis(cyclopeptide)

Poster Session & Conference Dinner Buffet

Tuesday, February 24, 2015, Morning Session

Dynamic Covalent & Systems Chemistry

08:00-08:50 *Keynote Lecture*
Sijbren Otto, Rijksuniversiteit Groningen, Groningen/NL
Systems Chemistry: From Molecular Recognition to Self-Replication

08:50-09:10 **Max von Delius**, Friedrich-Alexander-Universität, Erlangen/D
Orthoester Exchange: A Tripodal Tool for Dynamic Covalent Chemistry

Sensors & Receptors

09:10-09:30 **Frank Biedermann**, Karlsruhe Institut of Technology, Karlsruhe/D
Sensitive Detection of Neurotransmitters in Water and Biological Media with Remarkably Selective, Fluorescent Chemosensors

09:30-09:50 **Rebecca Sure**, Universität Bonn, Bonn/D
Supramolecular Association Free Energies by Dispersion Corrected Density Functional Theory

09:50-10:10 **Sascha Woitschetzki**, Universität Duisburg-Essen, Essen/D
Strongly underestimated dispersion energy in supramolecular complexes

Coffee Break

Functional Supramolecules I

10:40-11:00 **Stefan S. Jester**, Universität Bonn, Bonn/D
Supramolecular Nanopatterns of Organic Molecules

11:00-11:20 **Vladimir A. Azov**, Universität Bremen, Bremen/D
Light-controlled Macrocyclization of Tetrathiafulvalene with Azobenzene: Designing an Opto-electronic Molecular Switch

11:20-11:40 **Lutz Greb**, Université de Strasbourg, Strasbourg/F
Axle-change – Imines as molecular switches and motors

11:40-12:00 **Uli Lüning**, Universität Kiel, Kiel/D
Mechanical contributions to supramolecular chemistry: On transport and force measurements

12:00-12:20 **Thomas Schrader**, Universität Duisburg-Essen, Essen/D
Molecular Tweezers – from Supramolecular Chemistry to Alzheimer's Therapy

Lunch Break

Tuesday, February 24, 2015, Afternoon Sesssion

Functional Supramolecules II

13:50-14:40 *Keynote Lecture*
Stefan Matile, Université de Genève, Genève/CH
Supramolecular Systems at Work

14:40-15:00 **Pinaki Talukdar**, Indian Inst. of Science Education & Research, Pune/IN
Unimolecular and Supramolecular Artificial Ion Channel Systems

15:00-15:20 **Ulrike Kauscher**, Westfälische Wilhelms-Universität, Münster/D
Liposomes with supramolecular responsive functionalization

15:20-15:40 **Burkhard König**, Universität Regensburg, Regensburg/D
Functionalized Vesicles in Sensing and Catalysis

15:40-16:00 **Carsten Schmuck**, Universität Duisburg-Essen, Essen/D
From Gene Delivery to pH responsive Gels: Functional Supramolecular Systems

16:00-16:10 Closing remarks (Lützen/Schalley/Seiffert)

Lecture Abstracts

L01 – Optically triggering ultrafast bidirectional PCET inside a self-assembled Nanocage

Rahul Gera, Ankita Das, Ajay Jha and Jyotishman Dasgupta*

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**Email: dasgupta@tifr.res.in*

Photosystem II (PSII) carries out light-triggered multi-electron catalysis inside its protein core using a spatially optimized set of chromophores to achieve kinetic stabilization of redox intermediates. In order to mimic the iterative process of intermediate stabilization highlighted by PSII, we aspired to carry out proton-coupled electron transfer (PCET) event inside a nanocage. We used a water soluble electron deficient Pd_6L_4-nanocage[1] to encapsulate a water insoluble electron rich guest, 4-hydroxydiphenylamine. [2] Upon incarceration of the guest inside the host, a charge transfer (CT) band due to donor-acceptor interaction arises in the visible region. Subsequent to photoexcitation at the CT band an ultrafast bidirectional PCET reaction takes place in ~900 fs with a generation of a stable phenoxyl radical state (>10 ns) with high quantum yields.[2] The implication of our novel photochemistry paradigm will be discussed.

References:

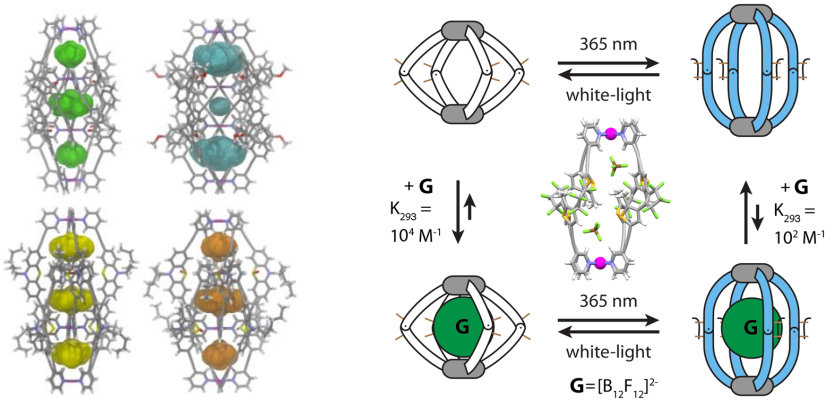
1. Y. Inokuma, N. Kojima, T. Arai, M. Fujita, *J. Am. Chem. Soc.* **2011**, *133*, 19691-19693.
2. R. Gera, A. Das, A. Jha, J. Dasgupta, *J. Am. Chem. Soc.* **2014**, *136*, 15909-15912.

L02 – Dynamics and Switching in Self-Assembled Hosts

S. Löffler, M. Frank, M. Han, R. Zhu, G. H. Clever*

**Georg-August University Göttingen, Department of Inorganic Chemistry, Tammanstrasse 4, Göttingen, Germany, E-mail: gclever@uni-goettingen.de*

Self-Assembled coordination cages are used for the recognition, transport and stabilization of small molecules.[1] Switchable host-guest systems promise to find application in fields such as uptake & release of molecular cargo, sensing and separation as well as catalysis inside confined molecular environments. Our current research efforts include the realization of non-trivial cage topologies and the implementation of dynamic control over the size and shape of the cages' internal cavities. Previously, we have reported a dibenzosuberone-based interpenetrated double-cage [$Pd_4Ligand_8$] which is capable of allosteric anion binding with a tremendous affinity for the inclusion of two chloride anions in its outer pockets.[2] The anion selectivity of the cages could be adjusted by the size of the template in the central pocket.[3] In contrast, another double-cage derivative was shown to bind neutral guests inside its central pocket upon activation with halide anions.[4] Yet another example allowed for switching of the cage architecture (monomeric vs. dimeric) by the addition of anionic triggers.[5] Based on this work, we recently showed, that the interpenetration principle can be extended onto other functional backbones such as the redox active compound phenothiazine.[6] By following another switching approach we showed that a photochromic coordination cage based on dithienylethene (DTE) ligands gives us full dynamic and reversible control over uptake and release of guests such as $[B_{12}F_{12}]^{2-}$ by irradiation with light of different wavelengths.[7]



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7. M. Han, R. Michel, B. He, Y.-S. Chen, D. Stalke, M. John, G. H. Clever, *Angew. Chem. Int. Ed.* **2013**, *52*, 1319.

L03– Stereoselective Self-Assembly of Chiral Metallo-Organic Cryptophanes

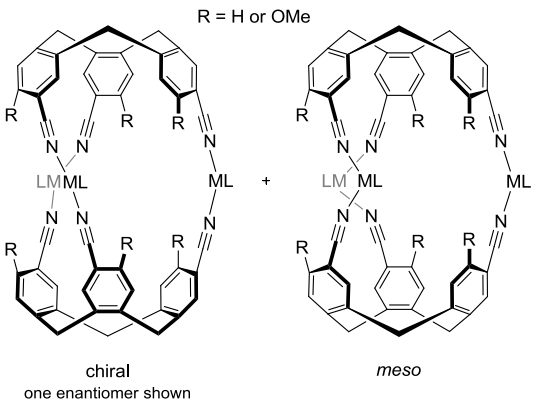
Astrid Schaly, Yoann Rousselin, Jean-Claude Chambron

Institut de Chimie Moléculaire de l'Université de Bourgogne (ICMUB, UMR CNRS 6302), Université de Bourgogne, 9 avenue Alain Savary, 21078 DIJON Cedex – FRANCE, Astrid.Schaly@u-bourgogne.fr

Self-assembly of organic compounds with transition metal cations has proven to be effective for the formation of molecular capsules and other two- or three-dimensional structures. Particularly molecular cages are of great interest because they possess a defined interior and can therefore act as hosts for molecular guests. Molecules such as calixarenes and cyclotriveratrylenes (CTVs) are widely used for the design of molecular cages due to their bowl-shaped structure and their rigidity. Since CTVs are chiral when the two substituents on the aromatic subunits differ, cryptophane-like metallo-organic assemblies exist in the form of two diastereomers, a *meso* form and a racemate.

Transition metal complex-assembled cryptophanes have first been described by Shinkai et al.[1] They used a pyridyl-functionalized CTV and mixed this with square-planar palladium(II) complex precursors affording a mixture of the *meso*- and the chiral (*P* and *M*)-forms of the corresponding cryptophanes. A similar approach by Hardie et al. involved the formation of a coordination cage from CTVs bearing remote 4-pyridyl substituents, which reacted with Pd(II) and Pt(II) complexes carrying *N*-donor chelating ancillary ligands such as ethylenediamine or 2,2'-bipyridine. The corresponding cryptophanes showed to be only metastable in solution and completely rearranged to the stella octangula cage in solution.[2] The use of stronger coordinating ligands like bis-*N*-heterocyclic carbenes stabilized the desired cryptophanes, which could be isolated as single *syn* isomers.[3] Other geometries like tetrahedral[4] or "Solomon's cube"[5] assemblies have also been observed.

This work describes a novel approach for the self-assembly of chiral cryptophanes, that involves racemic CTV derivatives carrying nitrile coordinating groups.[6] Reaction of these CTV ligands with appropriate Pd(II) or Pt(II) precursors leads to the diastereoselective formation of the chiral cryptophanes at room temperature, as shown by ^{1}H NMR spectroscopy and by XRD. In addition we found that the stereochemistry of these cryptophanes does not only depend on the binding unit attached to the CTV but also on the solvent used and the temperature of the solution as suggested by detailed NMR studies.



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3. J. J. Henkelis, C. J. Carruthers, S. E. Chambers, R. Clowes, A. I. Cooper, J. Fisher, M. J. Hardie, J. Am. Chem. Soc. 2014, 136, 14393-14396.
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[6] L. Peyrard, M.-L. Dumartin, S. Chierici, S. Pinet, G. Jonusauskas, P. Meyrand, I. Gosse, *J. Org. Chem.* **2012**, *77*, 7023-7027.

L04 – "Remote control" of stereoselectivity in C-C forming reactions in the periphery of hierarchically assembled helicates

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Hierachically assembled helicates are formed form very simple catechol ligands in the presence of titanium(IV) and lithium ions.[1] The stereochemistry of the complexes can be influenced by appropriate chiral substitutents. Thorough investigations reveal some unusual stereochemical effects.[2,3]

The use of mixtures of catechols leads to complexes with a more or less statistical distribution of the ligands. Such "libraries" of coordination compounds are used for the remote control of stereochemistry of C-C bond forming reactions at achiral moieties.

References:

1. M. Albrecht, S. Mirtschin, M. de Groot, I. Janser, J. Runsink, G. Raabe, M. Kogej, C. A. Schalley, R. Fröhlich, *J. Am. Chem. Soc.* **2005**, *127*, 10371-10387.
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L05 – Cobaltocene Mediated Reductive Coupling of Iminoboronates

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Subcomponent self-assembly exploits the reversible formation of covalent and coordinative bonds to prepare complex architectures from simple subcomponents, such as metal ions and organic ligands. A wide variety of architectures from helicates to tetrahedra and icosahedra can be assembled using this technique through the formation of imine bonds around metal centres.[1] The dynamic iminoboronate motif has also been exploited to produce macrocycles[2] and cages.[2b, 2c] Recently, it has been reported that iminochloroborane derivatives undergo reductive coupling to give dimers.[3] Herein, we report the mild reductive coupling of iminoboronates and investigate the formation of larger, self-assembled structures exploiting this reactivity.

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1. T. K. Ronson, S. Zarra, S. P. Black, J. R. Nitschke, *Chem. Commun.* **2013**, *49*, 2476-2490.
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L06 – Giant Boronic Ester Cages

M. Mastalerz

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In recent years shape-persistent organic cage compounds have evolved as soluble precursors for a new type of supramolecular permanent porous material.[1,2] In contrast to extended network materials, the porous units (molecular organic cages) are soluble and thus processable.[3] We showed that by exploiting reversible formation of boronic esters, giant mesoporous cages and catenanes with surface areas of up to 3758 m^2/g in the solid state are accessible.[4,5]

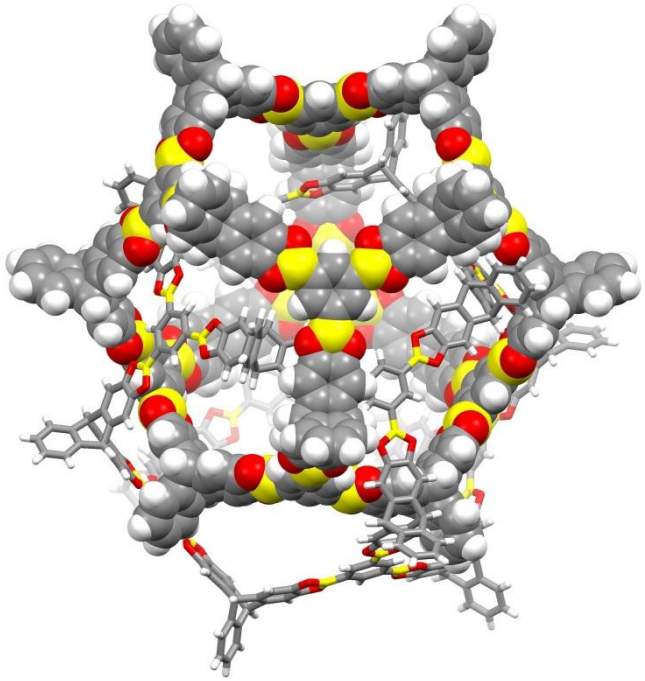

Figure 1. *Crystal structure of a giant cage catenane. Alkyl side chains omitted for clarity.*

References

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2. Mastalerz, M., *Synlett* **2013**, *24,* 781-786
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L07 – Shape-Controlled Synthesis and Self-Sorting of Covalent Organic Cage Compounds

S. Klotzbach, F. Beuerle

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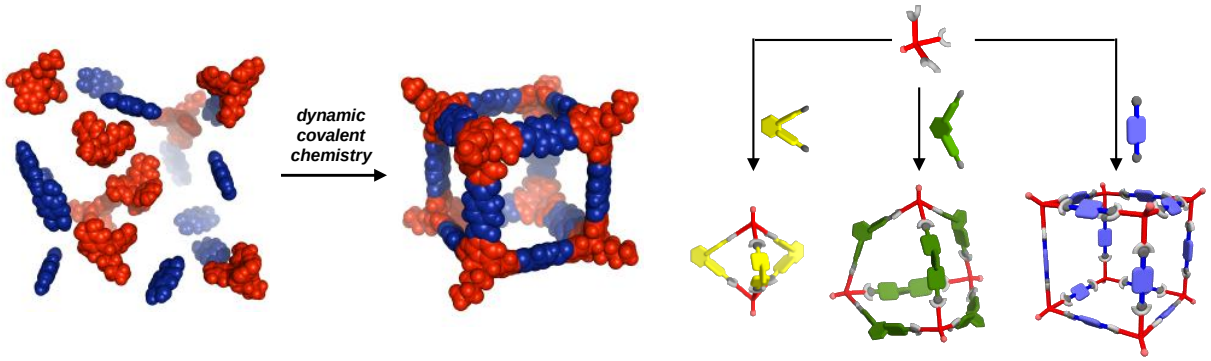
Covalent organic cage compounds are an intriguing class of molecular nanostructures and have drawn growing interest among chemists not only because of their structural beauty but also due to intrinsic properties such as well-defined cavities or shape-persistency making them promising candidates for porous functional materials.[1] Fashionable synthetic protocols for suchlike complex nanostructures generally utilize dynamic covalent conditions, where small organic building blocks in the right stoichiometry are cross-linked under thermodynamic control. However, prediction of the geometrical shape of the assemblies and product control for complex reaction mixtures is still a challenging task.

Here we report on the design, synthesis and characterization of a series of covalent organic cage compounds based on catechol-functionalized tribenzotriquinacenes (TBTQs). Co-assembly of the tritopic TBTQ units and ditopic diboronic acids with varying angular dispositions of the two reactive sites give rise to the efficient formation of monodisperse cage structures, whereby the geometrical shape and the stoichiometry of the assembly only depends on the angular disposition of the two boronic acids of the ditopic linkers. As predicted by the directional bonding approach,[2] the shape of the cage structures can be rationally switched from trigonal-bipyramidal A_2B_3 assembly to tetrahedral A_4C_6 cages or A_8D_{12} nanocubes[3] by simply changing the angular disposition of the diboronic acids from *ortho* to *meta* and *para*, respectively.[4] Furthermore, in the case of complex reaction mixtures containing two different boronic acids, both narcissistic self-sorting into separate cages as well as social self-sorting with novel three-component assemblies as the only detectable reaction product could be observed depending on the structure of the diboronic acids.



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4. S. Klotzbach, F. Beuerle, *to be submitted.*

L08 – Enzyme-like catalysis in self-assembled aromatic cavities

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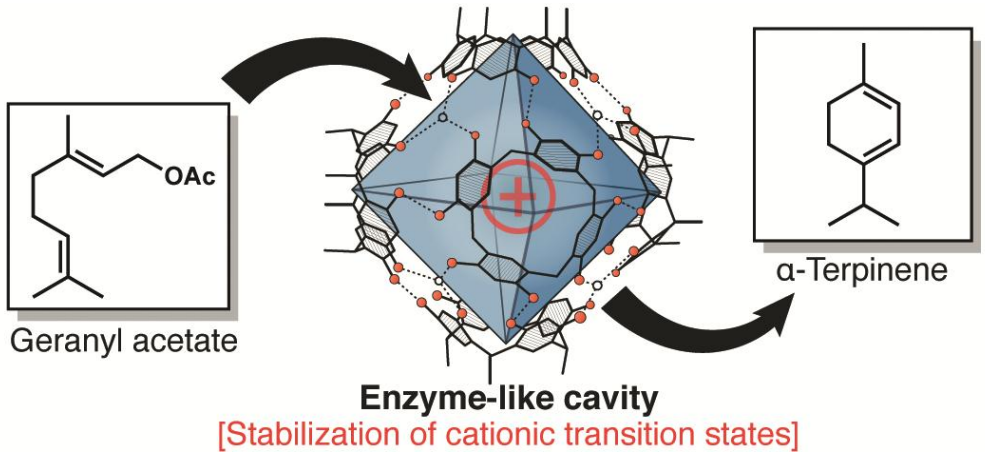
Nature's extraordinary elegance when performing chemical reactions has fascinated and inspired chemists for decades. Arguably, one of the most complex organic transformations performed in living organisms, is the tail-to-head terpene (THT) cyclization.[1,2] It allows the construction of the most diverse class of natural products, namely terpenes, *via* nature's way of combinatorial chemical synthesis. Thousands of different natural products are formed from just a handful of simple, acyclic starting materials: geranyl pyrophosphate (monoterpenes), farnesyl-PP (sesquiterpenes) and geranylgeranyl-PP (diterpenes). Nature utilizes enzymes, termed cyclases or terpene synthases, to carry out this complex transformation. Building upon our initial results,[3] we explore possibilities to utilize supramolecular structures to mimic such complex transformations in the laboratory. The latest results in this direction will be presented.[4]



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2. D. J. Miller, R. K. Allemann *Nat. Prod. Rep.* **2012**, *29*, 60.
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4. Q. Zhang, K. Tiefenbacher **2014**, under revision.

L09 – The Selective Entrapment and Degradation of Nerve Agents with Amino-Acid Containing Baskets and their Assemblies in Water

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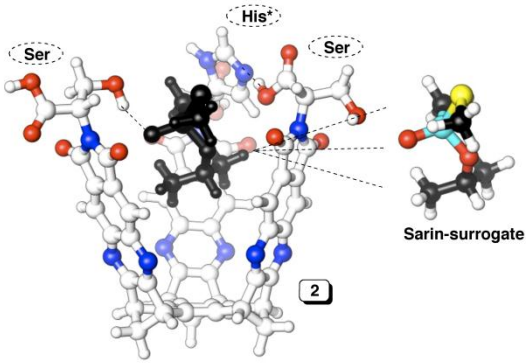
Biological molecules are complex and dynamic structures, yet some, such as organophosphorus hydrolase, butyrylcholinesterase and paraoxonase, are capable of neutralizing nerve agents. However, they are also fragile, expensive to produce on a large scale, and limited in possible options for reaction media. With the assistance of computational and experimental chemistry, we have been developing molecular baskets (see figure below) as models for examining the preparation of more advanced and robust synthetic substitutes of enzymes.[1] Since the degradation of nerve agents with enzymes starts with their encapsulation, we focused on understanding the recognition of numerous organophosphorus (OP) compounds akin to *G/V* type toxins. In particular, we placed amino acids of the same of different kind around a cup-shaped platform and measured the affinity of such hosts for trapping OP compounds in water.[2] Importantly, we have discovered that amphiphilic baskets assemble into stimuli-responsive vesicles capable of changing their shape/size upon encountering OP compounds in water.[3] The lecture will describe our recent efforts toward understanding the selective encapsulation of OP compounds and promoting their catalytic degradation.



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KL01 – Transformative Cages and Luminous Chains: Functional Materials Through Subcomponent Self-assembly

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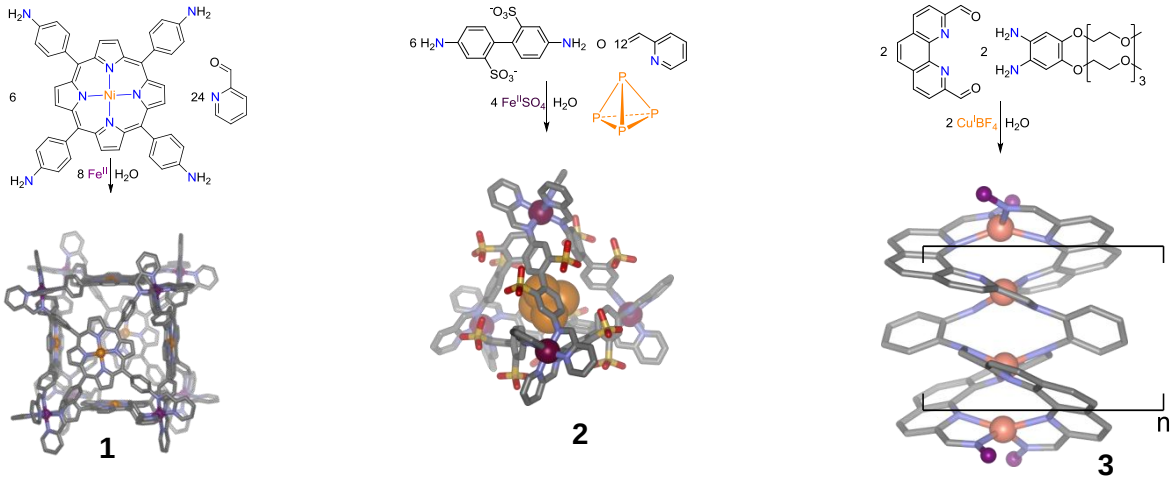
The materials that we depend on rely upon ever-increasing structural complexity for their function. The use of chemical self-assembly as a synthetic technique can simplify materials preparation by shifting intellectual effort away from designing molecules, and towards the design of *chemical systems* that are capable of self-assembling in such a way as to express desired materials properties and functions. This talk will focus upon the design of self-assembly processes that can bring together simple organic molecules and first-row transition-metal ions into complex, functional structures. Below are shown the subcomponent precursors and crystal structures of three of these products: Fe^{II}_8 cubic cage **1**,[1] Fe^{II}_4 tetrahedral cage **2**,[2] and white-light electroluminescent Cu^{I}_n double-helical polymer **3**.[3]



Where multiple structures are formed in parallel,[4] and in particular where structures act in concert to achieve a catalytic goal,[5] our techniques allow entry into the emerging field of *systems chemistry*.[6]

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KL02 – Metallo-supramolecular polymers

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Metallopolymers and metallosupramolecular polymers are interesting materials due to their combination of typical polymer properties with "metallic properties".[1] Additionally, the reversibility of the metal ligand interaction can be utilized for the fabrication of smart materials.

In recent years, we developed different synthetic pathways for the fabrication of metallo-supramolecular polymers. Functional initiators allowed the preparation of well-defined ligand containing polymers by living/controlled radical polymerization techniques.[2] These polymers have been utilized for supramolecular assemblies (*e.g.*, block copolymers, polymeric micelles, chain extended polymers). Linear metallopolymers have been synthesized by complexation of conjugated *bis*terpyridine ligands.[3] The choice of the conjugated ligand as well as the corresponding metal ion allowed the tuning of the optical properties of the resulting polymeric materials.[4] Moreover, controlled radical polymerization techniques (*e.g.*, RAFT) could be applied for the synthesis of functional polymers with different metal complexes in the side chain.

Metallo-supramolecular polymers feature an interesting behavior in solution, which was investigated by NMR spectroscopy as well as analytical ultracentrifugation (AUC).[2,5] Additionally, the conjugated metallo-supramolecular polymers as well as the side chain systems show interesting optical properties (*i.e.* energy transfer between donor and acceptor units).[4] Consequently, these materials are interesting candidates for light harvesting and hydrogen generation.[6] Furthermore, the reversibility of the metal ligand interaction (associated with an change of the optical properties) was utilized for the fabrication of sensor systems.[7] Another example for the utilization of the reversible interaction is the design of self-healing metallopolymers.[8]

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L10 – pH-Regulated Supramolecular Polymerisation

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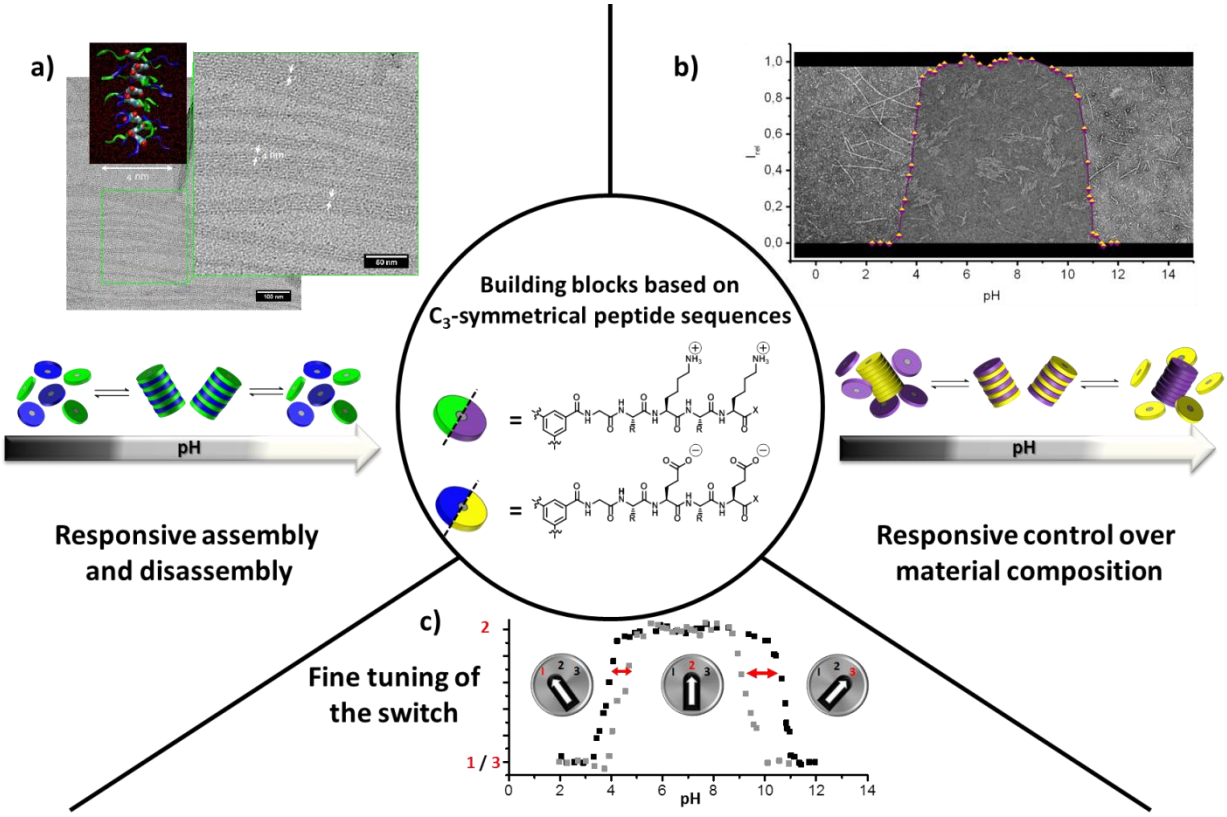
We aim to develop supramolecular synthons for the controlled self-assembly in water.[1-4] β-sheet-encoded anionic and cationic dendritic peptide amphiphiles form supramolecular alternating *co*polymers when self-assembled in a 1:1 feed ratio of the monomers. These ampholytic materials have been designed for on-off polymerization in response to pH triggers.[3] The self-assembly process is switched on at a physiologically relevant pH value and can be switched off by increasing and decreasing the pH value (a). Recent results on controlling the reactivity of supramolecular (*co*)monomers will be presented and discussed (b): the β-sheet-synthon dictates the pH transition at which the *co*polymer to monomer,[3] or *co*- to *homo*polymer occurs (c).[4] Furthermore we are currently exploring opportunities in the development of supramolecular (*co*)polymer brushes, via surface initiated pH-gradient techniques and sequence specific multicomponent polymerisations.



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L11 – Fullerene-Polyglycerol hybrids

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Freie Universität Berlin, Takustr. 3, 14195

Due to the unique structure and properties of fullerenes, their water soluble derivatives are of great interest for various applications such as transport of hydrophobic drug molecules into the tumors [1]. This work explains an efficient and easy way to synthesize water soluble fullerene-polyglycerol hybrids (Full-PG) with different physicochemical properties by using “graft-from” approach based on ring-opening polymerization of glycidol [2]. Full-PG hybrids with different number of polyglycerol branches and also those with different degree of polymerization were obtained using different ratios of fullerene to glycidol or different amount of anionic centers on the surface of fullerene respectively. They were able to form aggregates with special sizes in aqueous solutions depending on the number of polyglycerol branches conjugated on the surface of fullerene. UV-irradiation of aggregates led to core-crosslinked particles through [2+2] cycloaddition reactions between π-conjugated systems of cores. The synthesized hybrid nanomaterials can be used as vectors for photothermal, photodynamic and chemotherapy in the same time and therefore they are powerful tools for future cancer therapy.

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L12 – Seeded Supramolecular Polymerization of Perylene Bisimide Organogelator

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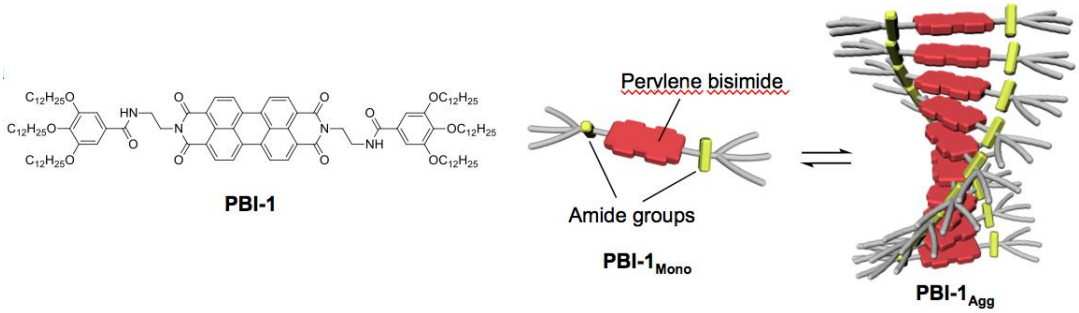
Kinetic control over supramolecular polymerization is the key for the design of functional nanostructures with similar sophistication as accessible in covalent polymerization. In this regard, seeded polymerization, as observed in actin and flagellin polymerization,[1] is a promising approach to obtain well-defined nanostructures. Here we show how the supramolecular polymerization by seeding approach[2] can be applied to π-conjugated systems based on perylene bisimide organogelator.[3]



In our current work the supramolecular polymerization mechanism of PBI-1 organogelator molecule has been investigated in detail from mechanistic viewpoints. This molecule self-assembles by the concerted hydrogen-bonding and π-π stacking interactions into highly defined one-dimensional helical nanofibers through a cooperative nucleation-elongation self-assembly process. Spectroscopic kinetic analyses provided novel insights into the polymerization process: a spontaneous nucleation is retarded by trapping of the monomers in an inactive conformation. The unique kinetics in the nucleation process was confirmed as a thermal hysteresis in a cycle of assembly and disassembly processes. Under appropriate solvent and temperature conditions within the hysteresis loop, we have succeeded in demonstrating seeded polymerization by addition of pre-assembled nanofiber seeds to the kinetically trapped monomer solution, enabling control of the time course of the supramolecular polymerization.

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L13 – Recognition of phosphates by synthetic receptors

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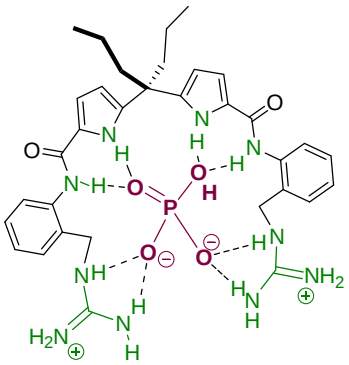
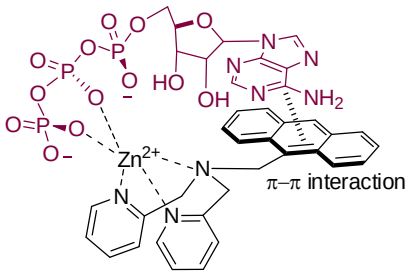
Selective recognition of anions by artificial receptors is still a great challenge in chemistry.[1] In our work, we focus on recognition and sensing of biologically relevant phosphates because they are an essential part of nature and living organisms. Understanding the principles how to bind and detect phosphates selectively in water is of great fundamental significance. We have investigated several approaches how to design receptors that bind phosphates selectively. Recently, we have designed receptor **1**, in which dipyrrolylmethane and guanidinium binding sites were combined.[2] The receptors show excellent selectivity for orthophosphate in aqueous buffer – methanol mixtures. We have investigated a structural mimetic of so-called "P-loop", which is found in most kinases and is responsible of phosphate recognition. Dipicolylamine-Zn(II)-based complexes, e.g. **2**, bearing aromatic dyes we have used to develop a selective probe for trinucleotides. Zn(II)-binding site and an aromatic dye are responsible for the coordination of the phosphate residue and the nucleobase, respectively. Such a combination has allowed us to achieve selectivity for adenine triphosphate.[3]



$\mathbf{1}^{2+}\bullet HPO_4^{2-}$



$\mathbf{2}^{2+}\bullet ATP^{4-}$

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L14 – Towards discrimination of carboxylates by hydrogen-bond donor anion receptors

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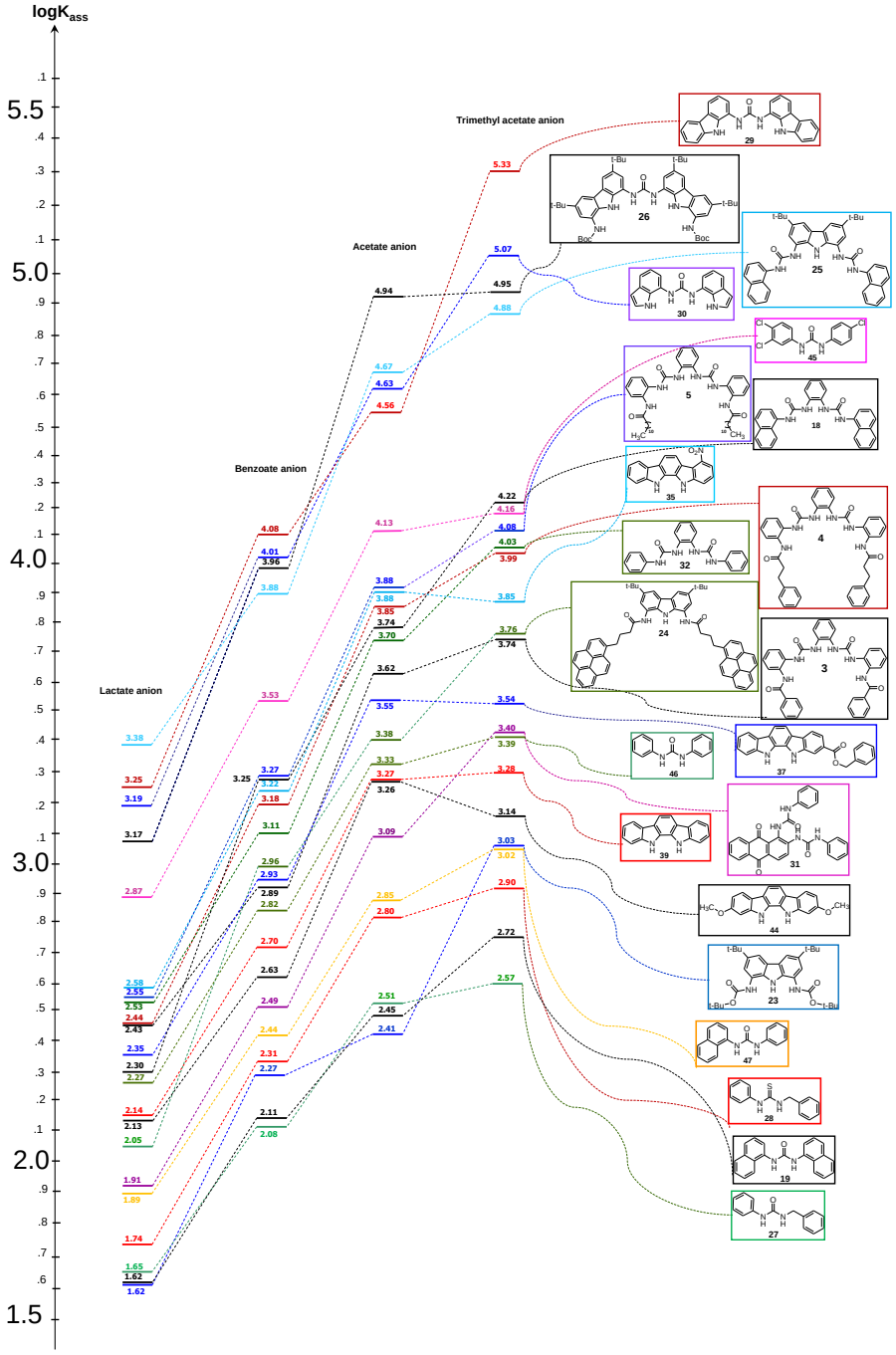
Binding constants (logK_{ass}) of small synthetic receptor molecules based on indolocarbazole, carbazole, indole, urea and some others, as well as their combinations were measured for small carboxylate anions of different basicity, hydrophilicity and steric demands – trimethylacetate, acetate, benzoate and lactate – in 0.5% H2O:[D6]DMSO using the relative NMR-based measurement method. Four separate binding affinity scales including 38 receptors were obtained (See scheme on the right). The binding strength is largely, but not fully, determined by the strength of the primary hydrogen bonding interaction. The latter in turn is largely determined by the basicity of the anion. Nevertheless, there are a number of occasions when the binding order changes with changing of the carboxylate anion. PCA reveals that this is primarily connected to preferential binding of trimethylacetate, supposedly caused by an additional hydrophobic/solvophobic interaction. These findings enable improved predictions regarding which receptor framework or cavity is best suited for carboxylate anions in receptor design.



L15 – The Chaotropic Effect: A Generic Driving Force for Anion Complexation

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Association phenomena in aqueous solution, whether between a macrocyclic host and an encapsulated guest or between a biological receptor and its corresponding substrate, are frequently accounted for in terms of a conglomerate driving force, the hydrophobic effect. Regardless of the precise description of the contributors to the hydrophobic effect,[1] it is intuitive that the tendency of a suitably sized guest molecule or residue to become encapsulated inside a hydrophobic macrocyclic cavity scales with its own hydrophobicity, which in turn relates inversely to its water solubility. Exceptionally large affinities can thus be reached, when highly hydrophobic adamantane, diamantane, or triamantane residues are employed as guest molecules.[2]

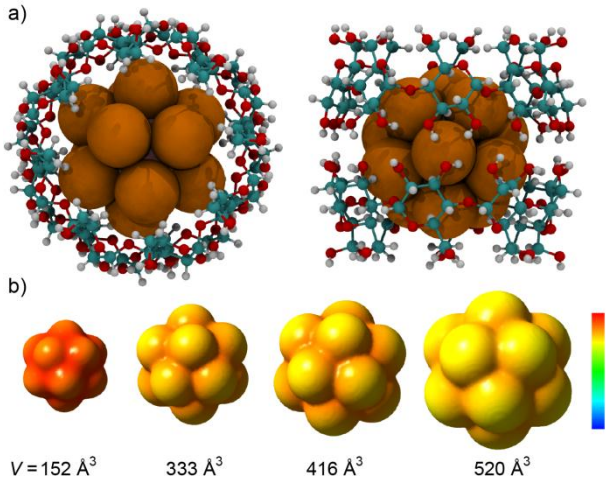

Figure. *a) Top (left) and side (right) views of the XRD structures of the inclusion entrapment of the $B_{12}Br_{12}^{2-}$ cluster into the γ-CD dimer. b) Size comparison and DFT-computed electrostatic potential maps for $B_{12}H_{12}^{2-}$, $B_{12}Cl_{12}^{2-}$, $B_{12}Br_{12}^{2-}$ and $B_{12}I_{12}^{2-}$.*

Dodecaborate anions of the type $B_{12}X_{12}^{2-}$ and $B_{12}X_{11}Y^{2-}$ (X = H, Cl, Br, I and Y = OH, SH, NR_3^+) form exceptionally strong (K_a up to 10^6 M^{-1}) inclusion complexes with macrocyclic hosts, γ-cyclodextrin (γ-CD) in particular. The micromolar affinities reached are the highest known for this native CD. The high driving force can be traced back to a *hitherto* underestimated driving force, the chaotropic effect, according to which chaotropic anions have an intrinsic affinity to hydrophobic cavities. In line with this argument, salting-in effects revealed dodecaborates as superchaotropic dianions. A new anchor motif (γ-CD●$B_{12}X_{12}^{2-}$) for diverse and orthogonal supramolecular applications is now at hand.

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L16 – Anion Binding by a Neutral Water Soluble Bis(cyclopeptide)

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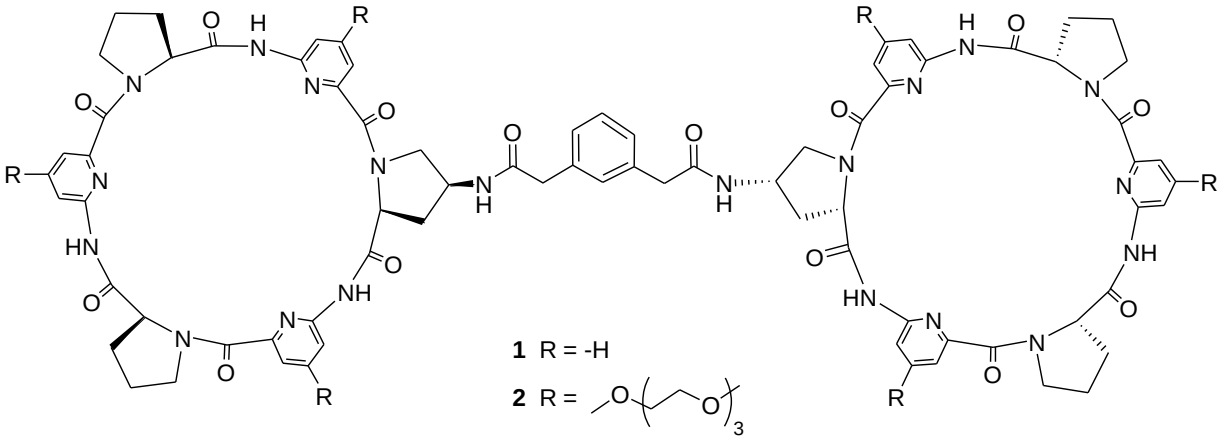
Our group recently described bis(cyclopeptide) **1** containing two cyclopeptide rings covalently connected via a 1,3-phenylenediacetic acid linker.[1] This compound possesses high affinity for sulfate anions in competitive aqueous solvent mixtures. Because of solubility problems the binding properties of **1** could only be characterized in water/methanol mixtures containing up to 50 % of water, however.



By introducing solubilizing groups into the aromatic subunits of **1** bis-(cyclopeptide) **2** could be obtained, which is soluble in water/methanol and water/acetonitrile mixtures up to 95 % water. Isothermal titration calorimetry revealed that **2** possesses the same affinity for anions in 50 % water/methanol as **1**, demonstrating that the additional substituents in **2** do not affect anion binding. Measurements in 95 % water/methanol demonstrate that anion affinity of **2** is high, even in this competitive solvent mixture.[2] In my presentation, the synthesis of **2** and the thermodynamic characterization of anion complexation in different water/methanol and water/acetonitrile mixtures will be discussed.

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KL03 – Systems Chemistry: From Molecular Recognition to Self-Replication

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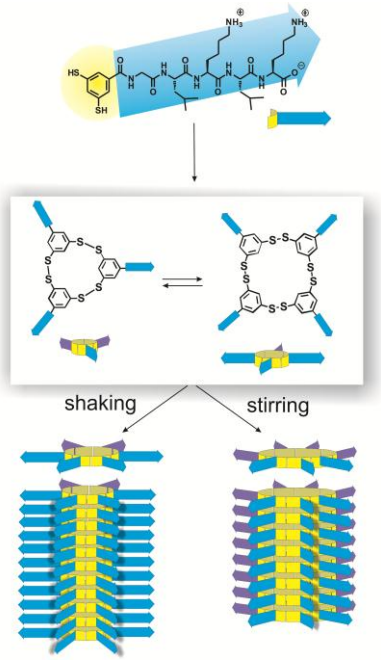
How the immense complexity of living organisms has arisen is one of the most intriguing questions in contemporary science. We have started to explore experimentally how organization and function can emerge from complex molecular networks in aqueous solution.[1] We focus on networks of molecules that can interconvert, to give mixtures that can change their composition in response to external or internal stimuli. Molecular recognition between molecules in such mixtures leads to their mutual stabilization, which drives the synthesis of more of the privileged structures.[2]

In this talk I will focus on two systems. The first is based on a single building block that gives rise to a small but unusually rich molecular network that can be induced to form catenanes (in the absence of any added template)[2a], a self-replicator (upon seeding), a catalyst (upon addition of its substrate), a synthetic receptor (upon adding a single template) and an allosteric receptor (upon adding two separate templates).



The second part of the talk will focus on self-replicating systems, where replication is driven by self-recognition of a molecule in the dynamic network.[3] Oxidation of a peptide-functionalized dithiol building block gives rise to a mixture of different-sized macrocycles. Stacking of the macrocycles into fibers may result in the autocatalytic production of more of this particular macrocycle at the expense of the other material in the molecular network. The selection rules that dictate which (if any) replicator will emerge from such networks are starting to become clear.

We have observed that factors such as mechanical energy (stirring or shaking) and the presence of cosolvents can determine which replicator wins the competition for building blocks. We have also witnessed a process akin to speciation in a system made from a mixture of two building blocks.

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L17 – Orthoester Exchange: A Tripodal Tool for Dynamic Covalent Chemistry

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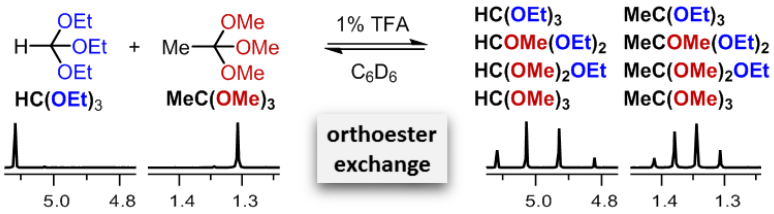
Dynamic covalent chemistry (DCC)[1] has developed into a powerful tool for probing non-covalent interactions, identifying ligands for medicinally relevant biotargets, and for synthesizing interesting molecules, (porous) materials, gels and polymers. Increasingly, dynamic covalent libraries (DCLs) are also being investigated from the perspective of the emerging field of systems chemistry.

In this talk, I will present our studies on a new tool for DCC: the acid-catalyzed exchange of *O*,*O*,*O*-orthoesters with alcohols.[2] We have demonstrated that orthoesters readily exchange with a wide range of alcohols under mild conditions and we have discovered that orthoesters engage in a metathesis reaction (Figure). We have also demonstrated that dynamic orthoester systems are prone to intriguing metal template effects, which can best be understood as agonistic relationships in a three-dimensional network. Due to the tripodal architecture of orthoesters, this exchange reaction has some advantages (and limitations) that are unique among all other processes currently used in the context of DCC.



Finally, I will present recent studies on possible uses of this new tool, including the one-pot synthesis of orthoester-based coronates and cryptates.[3]

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L18 – Sensitive Detection of Neurotransmitters in Water and Biological Media with Remarkably Selective, Fluorescent Chemosensors

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The creation of artificial receptors remains an open challenge in supramolecular chemistry and particularly the detection of small biomolecules in aqueous or complex biological media by supramolecular chemosensors proved difficult. Herein we provide a remarkably facile and versatile biomimetic strategy for the design of high-affinity artificial receptors by exploiting a combination of specific analyte-host interactions and the powerful, non-classical hydrophobic effect as driving forces for binding.[1] Specifically, we show that functional chemosensors can be obtained by a simple mix-and-match approach of suitable porous, inorganic framework materials and emissive dyes.[2] The potency of this novel design concept is exemplified for the sensitive detection (up to nanomolar) of medicinally important aromatic amine neurotransmitters serotonin, dopamine, norepinephrine and histamine (Fig. 1) with an outstanding selectivity over their natural amino acid precursors, and many other biomolecules. Importantly, the chemosensors were found to remain functional inside biological media such as blood serum and living cells. In addition, ratiometric sensing strategies and pattern recognition approaches are implementable. The non-destructive, reversible binding mode of the receptors, their modular design and the ease of their spatial localization provide countless application opportunities, for instance to monitor the uptake, release, (bio)synthesis and degradation of the neurotransmitters in real time, of which examples are provided in the talk.

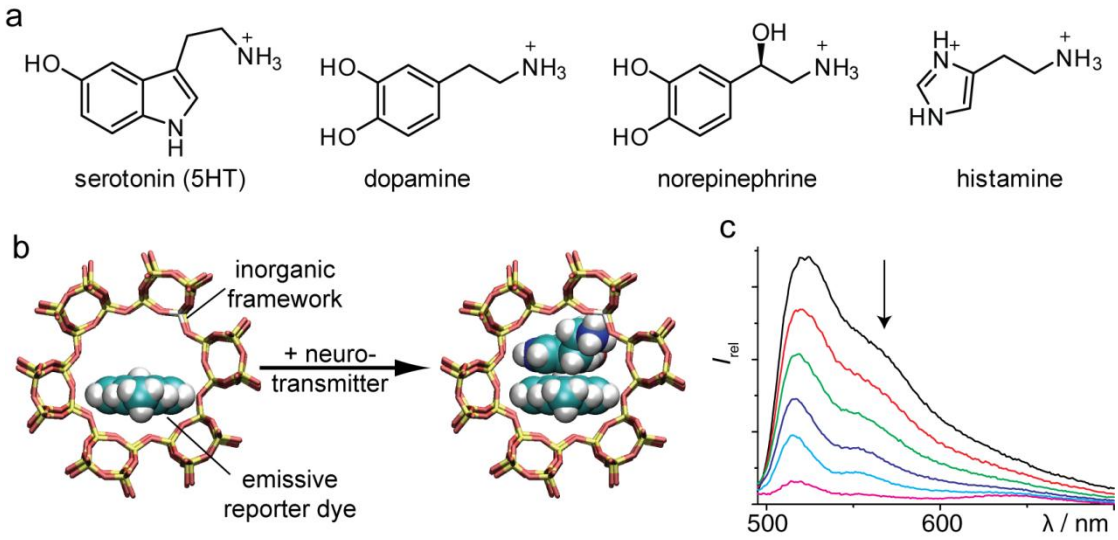

Figure 1: a) Aromatic neurotransmitters that can be selectively detected, even in the presence of up to 100.000 excess of their natural precursors, e.g. histidine or tryptophan. b) Chemosensors can be self-assembled from a emissive dye and a porous inorganic framework material. c) Characteristic changes in the emission intensity of the dye occur in the presence of the neurotransmitter.

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L19 – Supramolecular Association Free Energies by Dispersion Corrected Density Functional Theory

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Non-covalent interactions such as van der Waals forces or hydrogen bonding play a crucial role in the formation of supramolecular systems. Association free energies ΔG_a for many host-guest systems can be computed with good accuracy by dispersion corrected density functional theory together with a relatively large AO basis set. We have shown this recently for 12 standard supramolecular complexes (S12L)[1,2] and while participating in the SAMPL4 blind test challenge, where relative ΔG_a values were to be calculated for a cucurbit[7]uril host and 14 different protonated amine guest molecules[3].

This work aims at extending the S12L test set to 30 experimentally investigated complexes in order to cover a wider range of association free enthalpies and to include a broader variety of binding motifs, higher charges, and less rigid hosts. The new S30L set now contains host-guest systems with ΔG_a in the range from -1.4 to -24.7 kcal mol^{-1} which feature nonpolar dispersion, $\pi-\pi$ stacking, CH-π interactions, hydrogen bonding and charges from -1 up to +4.

The ΔG_a value at a given temperature in solution is calculated as the sum of the electronic association energy ΔE, the thermostatistical corrections from energy to free energy ΔG^T_{RRHO} in the gas phase and the solvation free energy ΔG^T_{solv}. In order to obtain a theoretical best estimate for ΔG_a we test several dispersion corrected density functionals to calculate ΔE, different semi-empirical methods to calculate ΔG^T_{RRHO} and use the continuum solvation models COSMO-RS and SMD to include the solvation contribution (ΔG^T_{solv}). Further, we investigate the effect of counter ions for the charged systems (S30L-CI set), which is found to significantly improve the results.

Our best method combination consists of PW6B95-D3/def2-QZVP' gas phase energies, HF3c[4] thermostatistical corrections and solvation free energies calculated with COSMO-RS. This combination yields a mean absolute deviation of only 3 kcal mol^{-1} for S30L-CI and a mean deviation of almost zero compared to experiment.

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L20 – Strongly underestimated dispersion energy in supramolecular complexes

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Noncovalent interactions play a pivotal role in molecular recognition. These interactions can be subdivided into hydrogen bonds, cation-π interactions, ion pair interactions and London dispersion forces. The latter are considered to be weak molecular interactions and increase with the size of the interacting moieties. Here we show that even the small chloroform molecule forms a very stable complex with a modified marine cyclopeptide. By means of high-level quantum chemical calculations, the size of the dispersive interactions is calculated; the dispersion energy (approximately 40 kcal/mol) is approximately as high as if the four outer atoms of the guest form four strong hydrogen bonds with the host. [1]

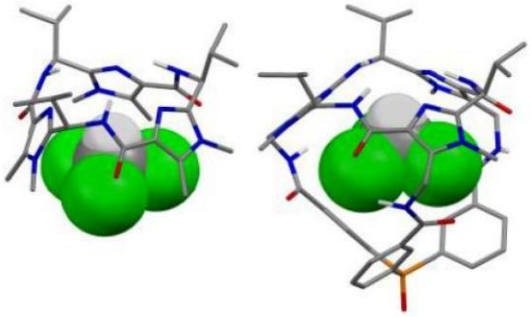

*Figure 1: Molecular structures of the complexes $CHCl_3$•**4** (left) and $CHCl_3$@cyclopeptide (right) was optimized using M05-2X/6-31G*,cc-pVTZ.*

However, these findings raised the question why the new complex of chloroform and the examined cyclopeptide shows a two orders of magnitude higher binding constants than the very similar cryptophanes by A. Collet et al. [2] Cryptophanes, composed of two bowl-shaped cyclotriveratrylene subunits linked by three aliphatic linker groups, are prototypal organic host molecules which bind reversibly neutral small guest compounds via London forces. The binding constants for these complexes are usually measured in tetrachloroethane and are in the range of 10^2 -10^3 M^{-1} . Here we show that tetrachloroethane is – in contrast to the scientific consensus – enclosed by the cryptophane-E cavity. By means of NMR spectroscopy we show that the binding constant for CHCl 3 @cryptophane-E is in larger solvents two orders of magnitudes higher than the one measured before. Ab initio calculations reveal that attractive dispersion energy is responsible for high binding constants and for the formation of imploded cryptophanes which seem to be more stable than cryptophanes with empty cavities. [3]

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L21 – Supramolecular Nanopatterns of Organic Molecules

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The self-assembly of organic molecules at the solid/liquid interface is an efficient approach towards two-dimensional architectures. These can be studied *in situ* with scanning tunneling microscopy, providing submolecularly resolved images. We recently described a set of shape-persistent macrocycles with dithiophene corners that are connected by alkoxy side chain substituted arylene-alkynylene sides. The molecules can be viewed as molecular polygons of triangular, quadratic, pentagonal, and hexagonal shapes that form supramolecular Archimedean tiling patterns (Figure 1) on graphite. The spontaneous cocrystallization of polygons with complementary symmetry leads to an extension of the lattice constants as compared to the individual compounds. In addition, the importance and informative value of microscopic techniques for the characterization of nanoscale compounds is highlighted, with examples from a variety of arylene/arylene-alkynylene systems such as bicyclophanes and molecular spoked wheels.

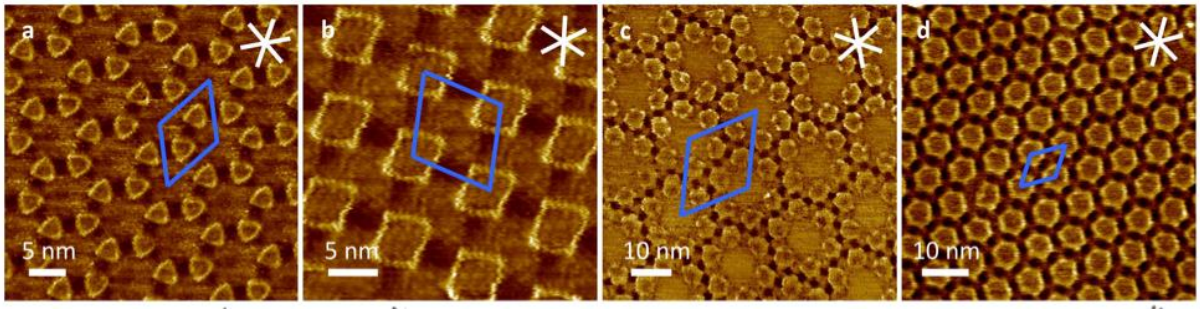

Figure 1: Scanning tunneling microscopy images of self-assembled monolayer patterns of molecular (a) triangles, (b) squares, (c) pentagons, (d) hexagons at the graphite/1,2,4-trichlorobenzene interface.

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L22 – Light-controlled Macrocyclization of Tetrathiafulvalene with Azobenzene: Designing an Opto-electronic Molecular Switch

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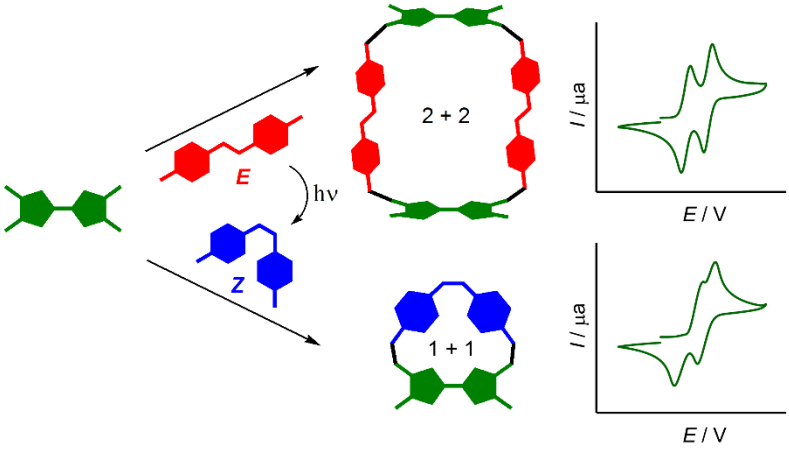
Visual perception is based on the transformation of a photon into an electrical signal via reversible *Z*—*E* isomerization of double bonds in a photochromic molecule. As a possible design for a simple molecular system capable of altering its electronic properties when exposed to light, we have considered molecular architectures containing tightly bound photochromic and redox active units within a rigid macrocycle. We have selected azobenzenes[1] (AB), versatile and easily tunable photoswitches, as optical modulators for our systems, and tetrathiafulvalenes[2] (TTF), redox active heterocyclic compounds displaying two consecutive reversible oxidation potentials, as possible electroresponsive units.



We have investigated macrocyclization between TTF dithiolates and *bis*-bromomethylazobenzenes/*bis*-bromomethylstilbenes under high dilution conditions and have shown that macrocycles of different size can be formed depending on whether the (*Z*)- or (*E*)-isomers of azobenzene or stilbene are used. This represents the first example of a light-controllable cyclization reaction. The oxidation potential of the small, structurally rigid, TTF-AB macrocycle is found to depend on the conformation of the AB moiety, opening the way for the modulation of redox properties by an optical stimulus. DFT calculations show that the out-of-plane distortion of the TTF moiety in this macrocycle is responsible for the variation of its oxidation potential upon photoisomerization of the neighboring AB bridge.

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L23 – Axle-change – Imines as molecular switches and motors

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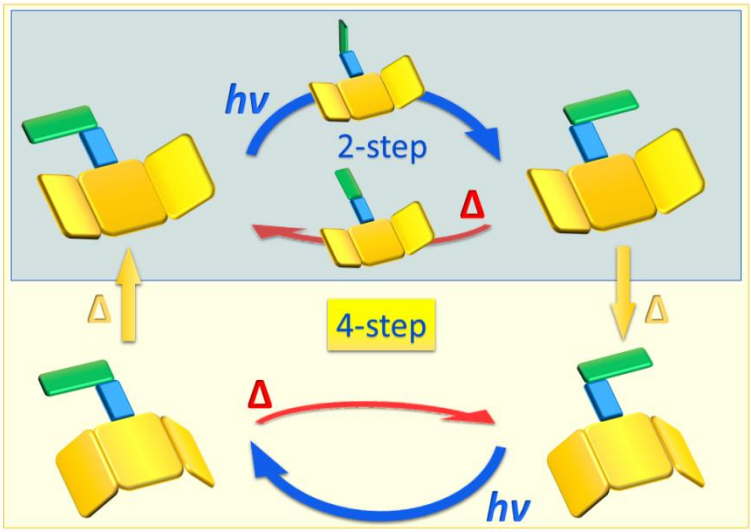
The capability of light-induced E/Z isomerization of simple imines (-N=C-), their ubiquity and their ease of preparation feature them as promising candidates for axle-functionalities in molecular switches and motors. Nevertheless, this class of compounds was mostly neglected for such purposes, possibly due to the thermal instability of the formed photoisomers.

After establishing some essential switching characteristics, we demonstrate that chiral N-alkyl imines undergo unidirectional rotation induced by light and heat.[1] Depending on the conformational flexibility of the stator part (the carbonyl residue) and the nitrogen inversion barrier of the rotor part (the amine residue) in the molecule, the operation mode of the motor can be considered as either a 4-step or a 2-step cycling motion of the rotor part.

The benefits of imines as molecular switches with potential extensions in different directions will be outlined.



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L24 – Mechanical contributions to supramolecular chemistry: On transport and force measurements

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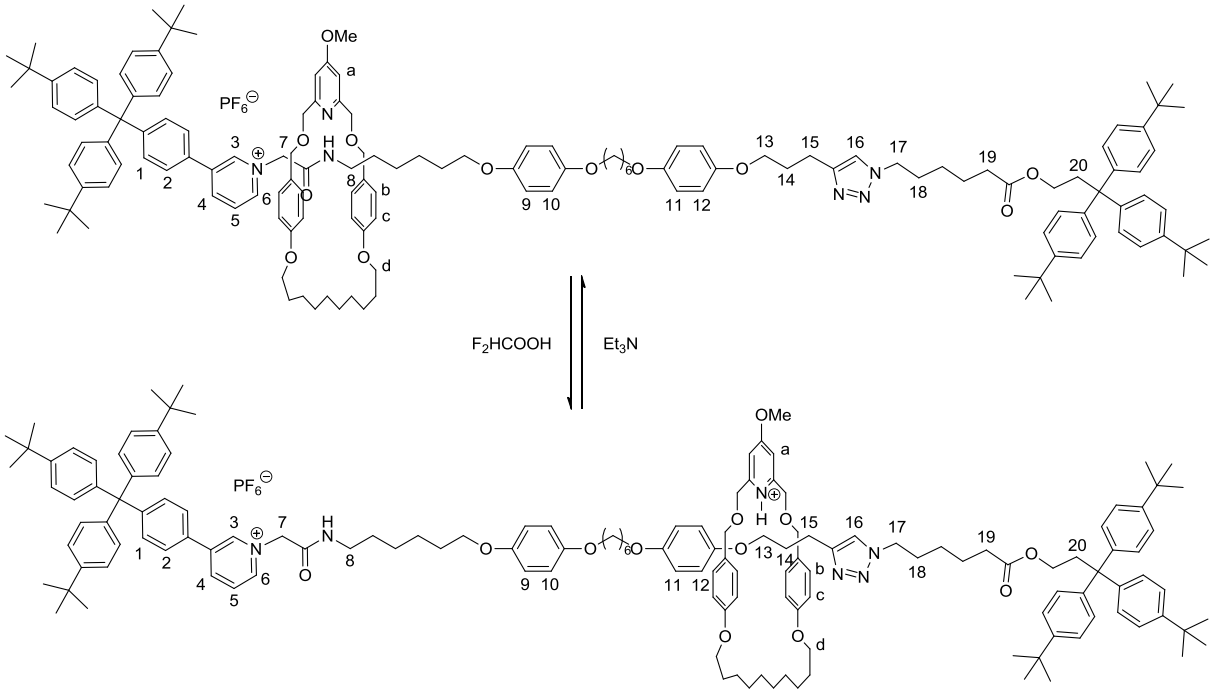
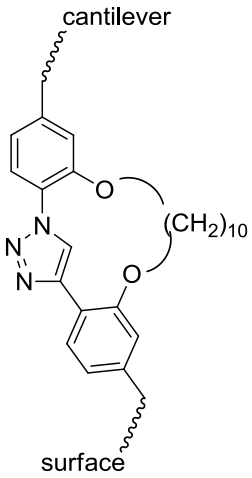
Mechanically interlocked molecules such as rotaxanes allow the movement of the ring along the axis without the problem of dissociation. This allows transport of for instance protons if the rotaxane's ring is protonable.[1]



How strong is a chemical bond, regardless whether covalent or supramolecular? Usually, quantitative measurements give dissociation energies in kJ/mol. On a single molecule level, however, one can determine the force (measured in pN) which is needed to break a bond by atomic force microscopy. Single molecules are attached to a surface on one side and to the cantilever on the other side and distance-force curves are measured. Eventually, the force is strong enough to break a bond. But which but will break? The talk present the safety line concept which is able to distinguish the rupture of central bonds in a molecule from detachment from the surface or cantilever. [2]



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L25 – Molecular Tweezers – from Supramolecular Chemistry to Alzheimer's Therapy

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Neurodegenerative diseases represent one of the unsolved medicinal problems of modern society – until today no cure for Alzheimer's and Parkinson's disease is available, and the number of patients increases dramatically.

In close collaboration with Frank Klärner, our group has in recent years developed a new family of receptor molecules for the amino acids lysine and arginine, with a unique threading binding mechanism, which operates at physiological conditions. These new supramolecular tools allow the deliberate interference with a large number of peptides and proteins. Noncovalent lysine/arginine complexation leads to selective shut-down of enzymatic activity, destruction of enveloped viruses and rescue of protein misfolding. The lecture presents most recent medicinal applications.

KL04 – Supramolecular Systems at Work

Stefan Matile

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This lecture with focus on synthetic supramolecular systems with interesting functions. The functions covered all emerged from an original interest on transport across lipid bilayer membranes. From there, sensors, photosystems and detectors for unorthodox interactions evolved as main lines of research. Focus will be on topics of current interest, with particular emphasis on the integration of unorthodox interactions into functional supramolecular systems. This will include catalysis with anion-π interactions, from Kemp elimination to enolate chemistry.[1] Existence and relevance of ionpair-π interactions on push-pull surfaces are elaborated by spectral tuning.[2] Up to three orthogonal dynamic covalent bonds are used in concert to construct functional surface architectures of highest possible sophistication with highest possible precision.[3] Ring tension is applied to dynamic covalent chemistry to find new ways to enter into cells.[4] Mechanosensitive bonds, finally are decisive for the development of new fluorescent probes that change color like lobsters during cooking and feel central characteristics of lipid bilayer membranes such as tension, potential and disorder.[5]

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L26 – Unimolecular and Supramolecular Artificial Ion Channel Systems

T. Saha, A. Roy, M. L. Gening, D. V. Titov, A. G. Gerbst, Y. E. Tsvetkov, N. E. Nifantiev, S. Dasari, D. Tewari, A. Prathap, K. M. Sureshan, A. K. Bera, A. Mukherjee, P. Talukdar*

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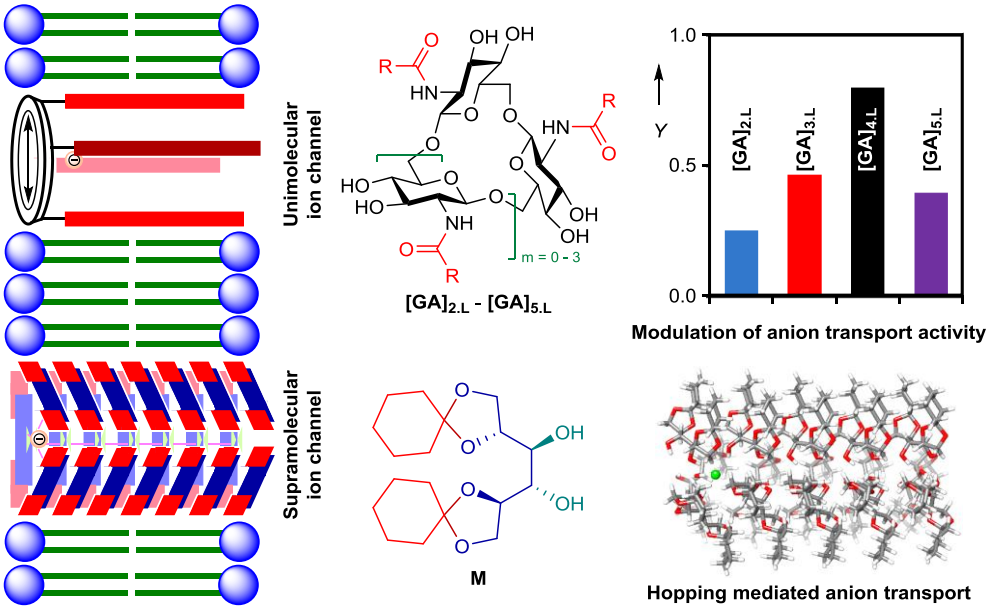
Selective transport of ion across biological membranes is facilitated by a certain class of biologically active channel forming proteins. Inspired by this, a large number of artificial ion channels have been created. Structural simplicity and chemical robustness have made these molecules as ideal candidates for mimicking the functions of their natural siblings. Functionalized cyclodextrins (CDs) have been used extencively in the unimolecular ion channel design.[1] However, inaccessibility of smaller CDs is a key limitation for manipulating the ion transport activity based on this system. New artificial ion channels (**[GA]$_{2.L}$-[GA]$_{5.L}$**) were designed based on oligo-(1→6)-β-*D*-glucosamines consisting of polar cavities.[2] The ion transport activity of these molecules relates the size of each macrocycle to its rigidity. We also have designed supramolecular-rosette ion channel by amphiphilic mannitol derivative **M**.[3] The free hydroxyl groups the mannitol derivative play dual roles by favoring the self-assembly process and anion recognition via hydrogen bonding interactions. The anion selectivity within the supramolecule was investigated by fluorescence-based vesicle assay and planar bilayer conductance measurements. Molecular dynamics simulation studies suggested an anion hopping mechanism favored by the relay transfer of the ion from one rosette to the next.



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L27 – Liposomes with supramolecular responsive functionalization

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Unilamellar vesicles are versatile tools for biomimicry applications, being specifically used to study diverse mechanisms taking place at the cell surface. Such mechanisms are usually responsive to external stimuli, e.g. an increase in temperature. Here we demonstrate how, respectively, light irradiation and a change of the redox potential trigger a change in the characteristics of liposomes.

We describe light-responsive vesicles that release their contents in response to a light-sensitive molecular trigger. To this end, liposomes were equipped with amphiphilic β-cyclodextrin that was covalently labelled with azobenzene. This innovative method is a promising approach towards specific targeting and non-invasive content release upon an external light stimulus. Using dye encapsulation and confocal laser scanning microscopy, we show that the permeability of these vesicles strongly increases upon UV irradiation (λ = 350 nm) with concomitant isomerization of apolar trans-azobenzene to polar cis-azobenzene on the liposome surface. Additionally, our system confines a light triggered receptor-unit on the liposome surface.

Redox-responsive vesicles are described on the basis of tetrathiafulvalenes (TTF). These remarkable redox active molecules are easy to oxidize, but strongly hydrophobic and therefore not soluble in aqueous solution. We show that the immobilization on the surface of liposomes via a cholesterol anchor gives the opportunity to oxidize and reduce the TTF-units stepwise in water. Moreover metastable $(TTF^{+\cdot})_2$-dimers are forming on the vesicle membranes and are further stabilized by a change of the membrane properties and addition of Cucurbit[8]uril.

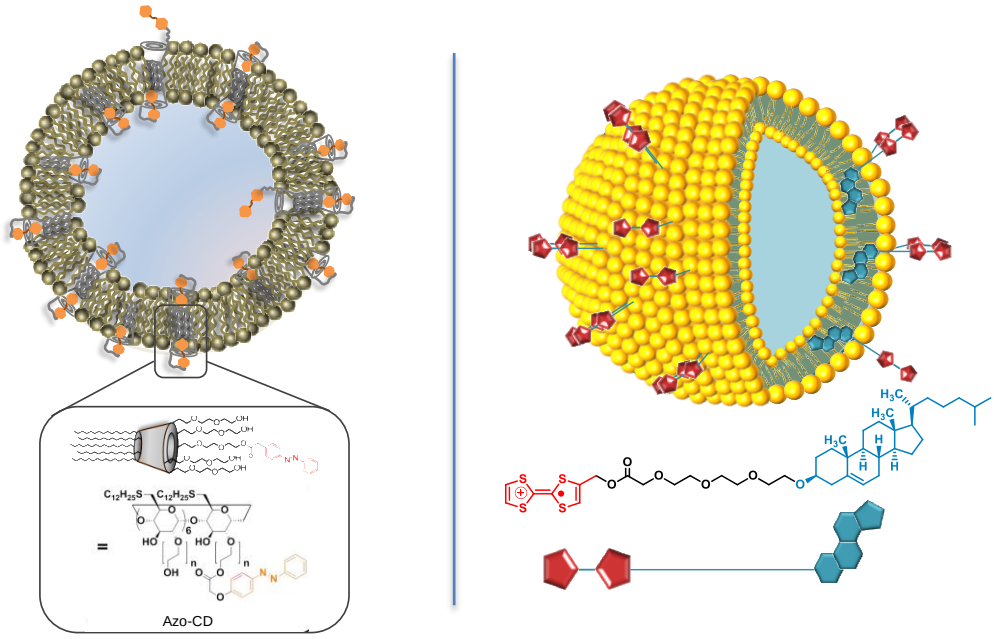

Figure 1: Schematic representation of light -/redox-responsive liposomes.

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L28 – Functionalized Vesicles in Sensing and Catalysis

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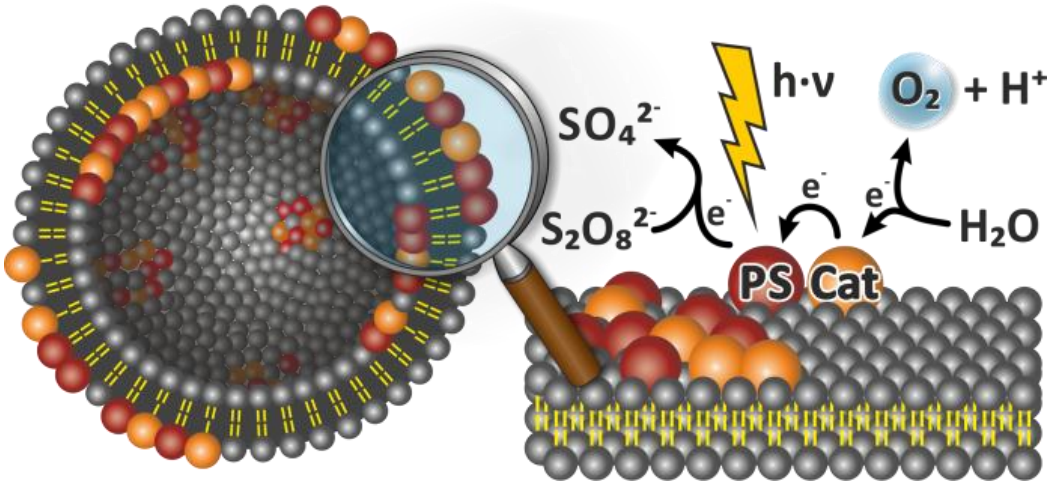
Co-embedding of amphiphilic molecules into the fluid membrane of stable 100 nm size vesicles has developed into a valuable strategy to enhance synergistic and cooperative effects in sensing and catalysis.[1] Luminescent indicators were obtained from amphiphilic receptor and reporter dyes, which self-assemble in vesicle membranes and signal the presence of a target analyte, such as ATP, pyrophosphate, peptides,[2] or monitor enzymatic conversions[3] by changes in their emission intensity. With diacetylene based lipids the vesicle surface was molecular imprinted in the presence of a template increasing the binding specificity.[4]

However, the same concept applies to synergistic catalysis: Catalyst and co-catalyst or sensitizer are co-embedded into the lipid vesicle membrane. The close proximity and two-dimensional, dynamic arrangement leads to an increased catalytic performance as observed in photocatalytic water oxidation[5] and ester hydrolysis.[6]



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L29 – From Gene Delivery to pH responsive Gels: Functional Supramolecular Systems

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Our research focuses on the development, synthesis and evaluation of new supramolecular systems which function in polar solvents and thus might have prospect for applications. Currently our work mainly involves ionic interactions as a key non-covalent bond. We have introduced guanidiniocarbonyl pyrroles as one of the most efficient oxoanion binding motifs known so far relying on H-bond assisted ion pair formation.

With the help of combinatorial approaches, we have used this binding motif to develop sensors for amino acids or highly efficient stereoselective receptors for oligopeptides. Currently, we are working on protein surface or DNA recognition. For example, tetravalent peptide ligands identified from the screening of a combinatorial library were shown to be highly efficient non-competitive enzyme inhibitors working by binding to the protein surface thus blocking the access to the active site. We also found a new class of DNA-binding molecules which function as very efficient artificial transfection vectors.

We are also interested in self-assembling zwitterions which form soft materials such as vesicles, polymers or monolayers in polar solvents and on surfaces. For example, recently we developed a supramolecular polymer based on a monomer with two orthogonal self-complementary binding sites using either metal-ligand or ionic interactions. In a hierarchical self-assembly process this molecule first forms ion paired dimers which can be polymerized by the addition of metal ions. Such system can also lead to the formation of pH-switchable gels.

Poster Abstracts

P01 – Hydrogen bonding and dispersion interactions within pseudo rotaxanes

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We present a theoretical study of the influence of anions on supramolecular binding in rotaxanes. Rotaxanes are molecules that consist of two noncovalently interlocked components, the wheel and a penetrating axle. Bulky stopper groups at the axle prevent unthreading of the ring. Such systems are of particularly interest, because of their potential use as molecular switching elements or even molecular shuttles. The macrocycle can rotate around the axle, or it can slide along its axle from one side to another.

We examined the binding pattern within hydrogen bonded pseudo rotaxanes of the Vögtle-Schalley-type where different diketopiperazine axles are placed in the cavity of a tetralactam macrocycle[1], see Figure 1. Here, we studied to which extent the hydrogen bond pattern is changed when anions like chloride are added and we discuss the influence on a potential shuttling within thepseudo rotaxane. The hydrogen bond strength is estimated on the basis of calculated IR-spectra.[2]

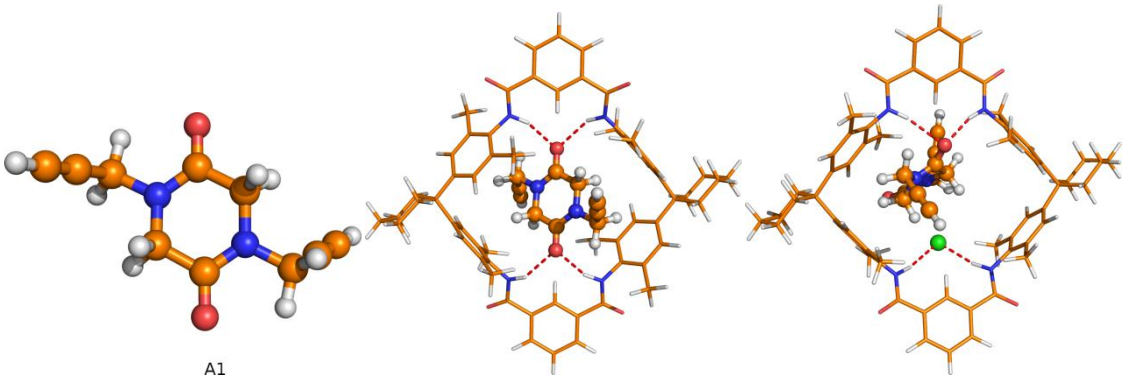

*Figure 1: Middle: The diketopiperazine axle **A1** is threaded in a tetralactam macrocycle. Left: Addition of chloride causes a partial hydrogen bond breaking*

It is well known that besides hydrogen bonding also dispersion interaction is crucial for rotaxanes[3] and other supramolecular systems. Therefore, the whole study was performed with density functional theory (DFT) calculations in combination with a dispersion correction (DFT-D3).[4] This approach enables us to study the influence of dispersion interaction for such large systems.

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P02 – Tuning the pH-triggered self-assembly of dendritic peptide amphiphiles via fluorinated side chains

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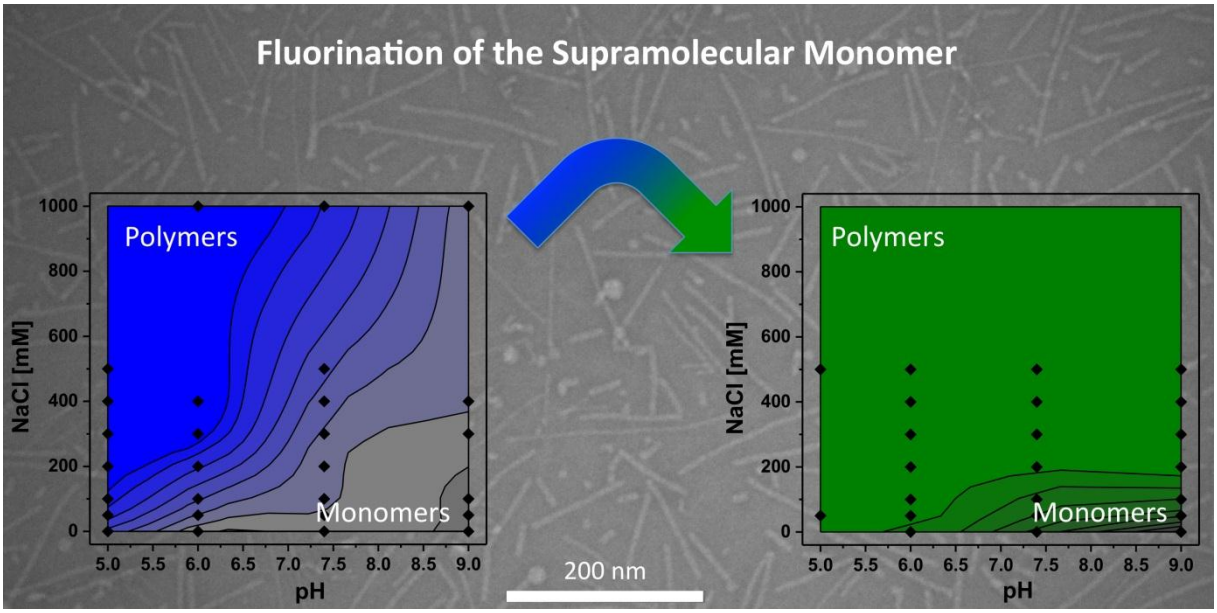
Recently, we have developed supramolecular materials that are designed for on-off polymerisation in response to pH-triggers. The self-assembly from small molecules into large polymeric nanorods is switched off in neutral pH and at physiological ionic strength, due to charge-charge repulsive interactions of deprotonated carboxylic acid moieties embedded in the amphiphilic peptides. Only when these negative charges are screened by lowering the pH, the thermodynamic driving force coded in the hydrophobic peptide segment of the molecules is turned on and thus leads to the formation of hydrogen bonded polymeric nanorods. Here we have prepared dendritic peptide based amphiphiles, which self-assemble into supramolecular polymers. The facile synthesis of fluorinated side chains increases the hydrophobicity of the peptidic backbone sequence, which has able us to tune the pH-switch in the aggregation of the peptide amphiphiles in water. The self-assembly from monomeric to polymeric state is induced by pH or ionic strength and can be followed by circular dichroism titration experiments and TEM imaging.



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P03 – Synthesis of a rotaxane with an unsymmetrical axis

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The design of artificial transmembrane channels has been widely investigated in organic chemistry.[1] In order to make these channels usable for sensors or molecular machines, they have to be able to undergo a directional motion. Rotaxanes, in which a wheel is threaded onto an axis with blocking groups on the ends, are very promising for this purpose because the ability of the wheel to slide along the axle can be influenced by an external stimulus.[2]

Therefore, we designed an acid-base switchable rotaxane that consists of a non-symmetrical axis with a cholesterol blocking group and a dibenzo-24-crown-8 wheel. The synthesis of this rotaxane will be presented.

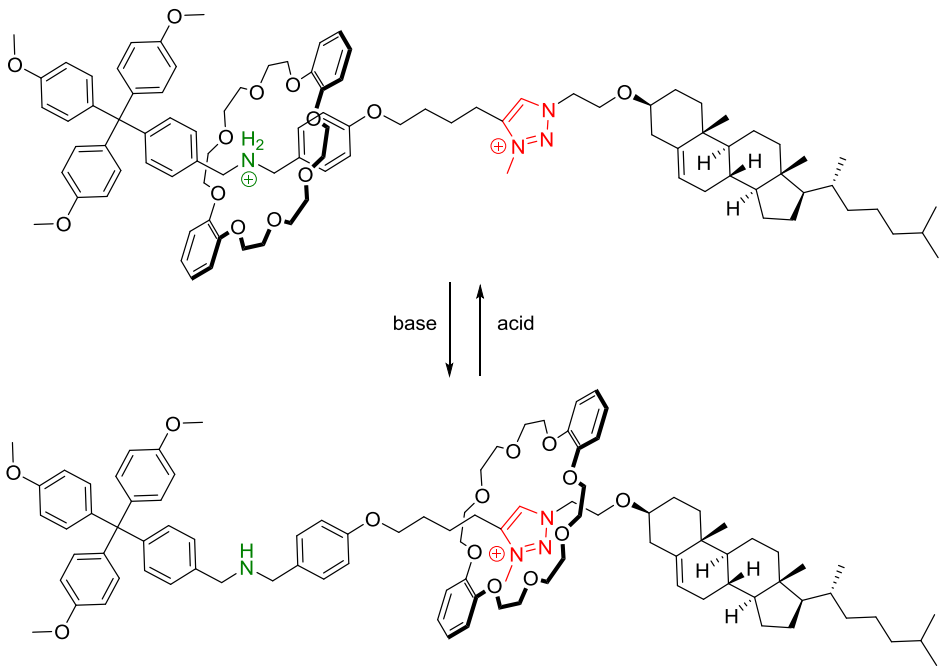

***Figure 1**. Structure of the [2]rotaxane with a permanent (red) and a pH dependent (green) binding site.*

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P04 – A [2]rotaxane shuttle with a fluorous ponytail for proton transport

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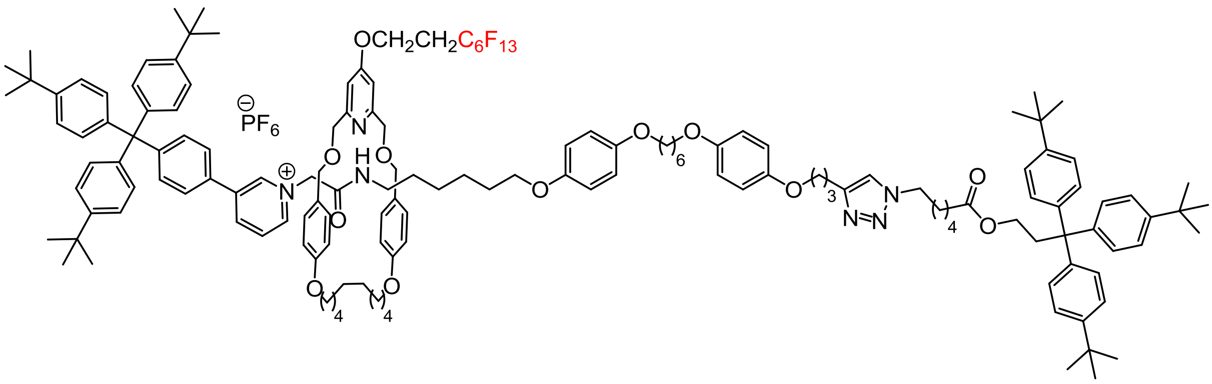
For the development of light-driven proton pumps, several [2]rotaxane shuttles carrying a pyridine macrocycle as a ring were designed and synthesized.[1] By protonation, a Coulomb repulsion between the positive charge of the protonated pyridine and an implemented positive charge in the axis leads to a movement of the protonated pyridine macrocycle. This means, the position of the pyridine macrocycle depends on the pH value. The first [2]rotaxanes were obtained in only low yields because of synthetic and purification problems. While the synthetic problems could be solved by using an excess of the costly educts, the purification problem remains because of the similar behavior of the [2]rotaxane and free axis.

Fluorous solid phase extraction (FSPE) is a well-known method to separate fluorous compounds from each other or from non-fluorous compounds.[2] By introducing a fluorous ponytail into the ring of a [2]rotaxane, a separation of the fluorous [2]rotaxane and the non-fluorous free axis on fluorous silica gel should be possible.

Therefore, a pyridine macrocycle with a fluorous ponytail was synthesized. The fluorous [2]rotaxane was obtained by trapping the fluorous pyridine macrocycle via copper catalyzed “click” reaction of an azide halfaxis and an alkyne halfaxis. Variation of the pH showed similar behavior for the fluorous and the related non-fluorous [2]rotaxanes, which means it can be used for proton transport. Due to the fluorous group at the macrocycle, a different elution behavior of fluorous [2]rotaxane and free axis could be observed on fluorous silica gel.



Scheme 1: *Fluorous [2]rotaxane for proton transport.*

References

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P05 – Synthesis of Substituted Conductive Diarylethenes for Connection with a Supramolecular Recognition Domain

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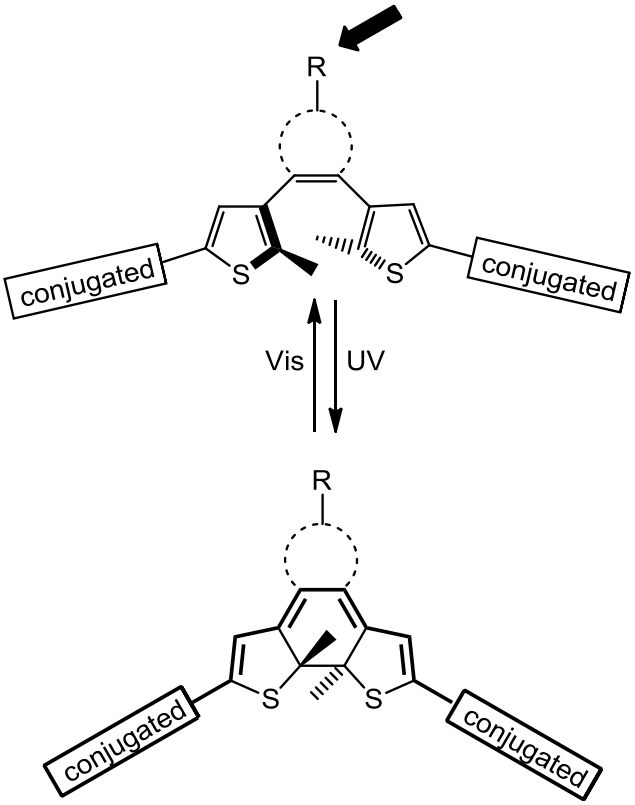
Diarylethenes which contain five-membered heterocyclic rings are well known as photochromic compounds that are thermo-irreversible, have high sensitivity and fatigue resistance properties. In contrast to the open twisted form, the π-system is completely conjugated in the closed isomer. The result is a decrease of the HOMO-LUMO gap and consequently the increase of conductivity by the molecule.



For switchable supramolecules, the switching unit must be connected with supramolecular recognition domains. In the case of a diarylethene, three sites can be further functionalized, the two ends of the "arms" at the thiophen units and the central alkene ring. In this poster, an approach to substitute the often used perfluorinated cyclopentene by an imidazole segment is discussed.

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P06 – Controlling Liquid Crystalline Phases by Host Guest Chemistry of Amphiphilic Cyclodextrin

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There are a few examples of amphiphilic cyclodextrins forming a liquid crystalline phase in literature. These systems only exhibit liquid crystalline phases at high temperatures[1] or the cavity of the cyclodextrins is sterically hindered[2]. The novel amphiphilic cyclodextrin presented in this work was synthesized in a five-step synthesis and the liquid crystalline properties were analyzed with Differential Scanning Calorimetry (DSC), Polarized Optical Microscopy (POM) and X-ray Diffraction (XRD) measurements. The amphiphilic cyclodextrin forms a lamellar liquid crystalline phase at moderate temperatures. Addition of different multivalent guest molecules lead to different liquid crystalline phases, which makes this system unique. To the best of our knowledge, this is the first example of a liquid crystalline cyclodextrin which is able to undergo host guest interactions. Future focus will lay on the investigation of stimuli responsive guest molecules like azobenzene or ferrocene. In this case a change in the structure could be triggered by UV irradiation or redox reactions.

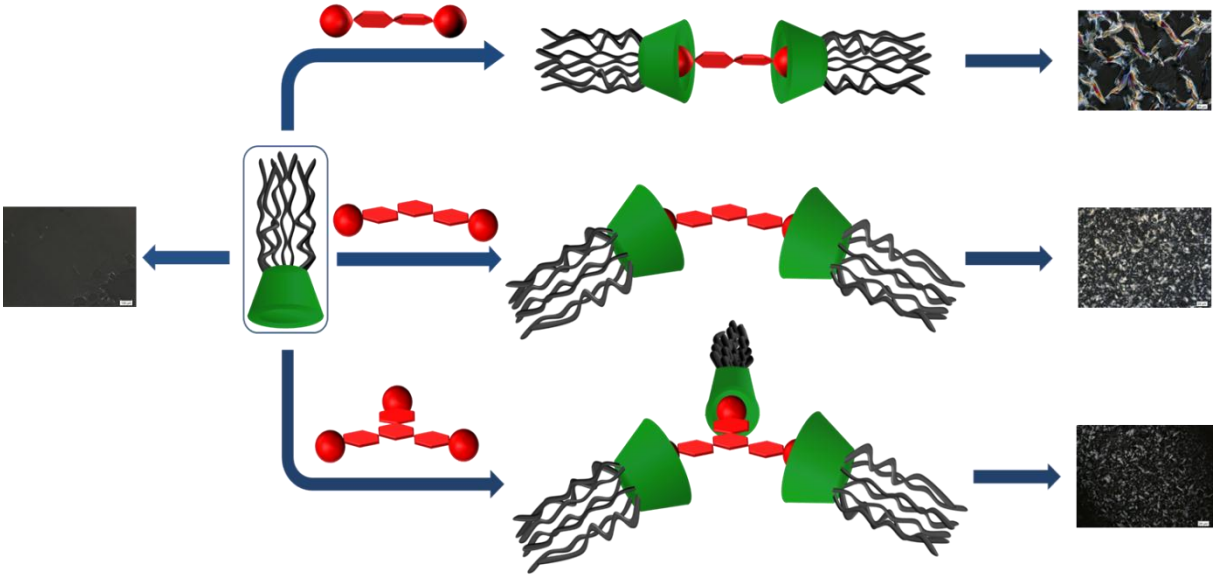

Figure 2: Schematic representation of the host guest system and POM images to show the change of the liquid crystalline phase.

References:

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P07 – Immobilization of Enzymes by Microcontact Printing and Thiol-Ene Click Chemistry

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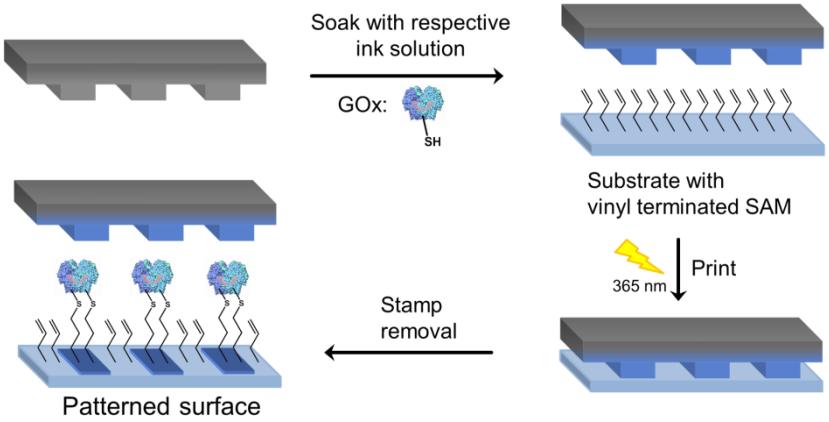
Microcontact printing in combination with thiol-ene click chemistry is an easy and fast technique[1]. This procedure is very cost efficient due to the small amount of compound needed. The mild conditions during the performance of this method allow the application of sensitive molecules like peptides and enzymes. The functionalization of surfaces with biomolecules is of great interest for the generation of bioactive and biocompatible materials.



In this study microcontact printing was used to functionalize a vinyl terminated self assembled monolayer (SAM) with cysteine modified RGD. The latter is a well known amino acid sequence that appears in proteins of the extracellular matrix. Specific receptor proteins on cell membranes bind to this sequence and RGD funtionalized surfaces are suitable for cell adhesion studies. Additionally, we were able to immobilize the enzyme glucose oxidase (GOx) and lactase (Lac). The first enzyme catalyzes the oxidation of glucose to gluconic acid and is widely used in the field of glucose sensors. Lac catalyses the cleavage of lactase in its components glucose and galactase. The coupling was verified by XPS, condensation experiments and fluorescence microscopy. The activity of the surface bound biomolecules was positively tested after immobilization to verify the successful binding of these enzymes in their active form.

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P08 – Stimuli-Induced Folding Cascade of a Linear Oligomeric Guest Chain Programmed through Cucurbit[n]uril Self-Sorting (n = 6, 7, 8)

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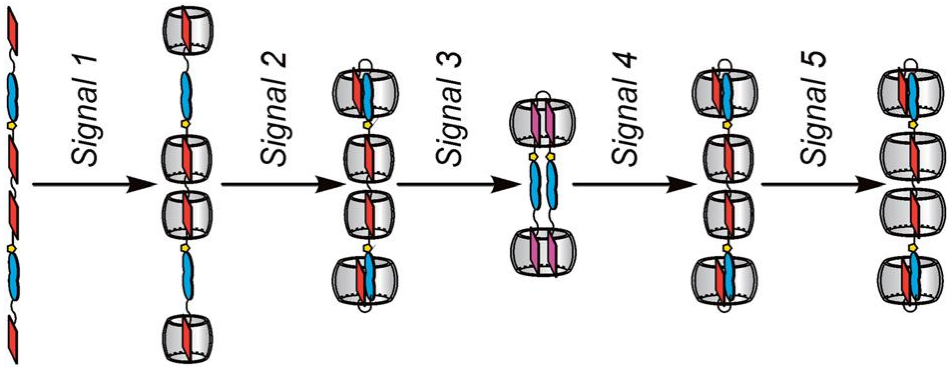
A six-station linear guest for cucurbit[7]uril and cucurbit[8]uril has been synthesized in order to implement a cascade of transformations driven by external stimuli. The guest chain is sequence-programmed with electron-deficient viologen and electron-rich naphthalene stations linked by either flexible or rigid spacers that affect the chain's folding properties. Together with the orthogonal guest selectivity of the two cucurbiturils, these properties result in self-sorted cucurbituril pseudorotaxane foldamers. Each transformation is controlled by suitable chemical and redox inputs and leads not only to refolding of the guest chain, but also to the liberation of secondary messenger molecules which render the system presented here reminiscent of natural signaling cascades.



The steps of the cascade are analyzed by UV/Vis, 1H NMR and electrospray (tandem) mass spectrometry to investigate the different pseudorotaxane structures in detail. With one guest oligomer, three different cucurbiturils, and several different chemical and redox inputs, a chemical system is created which exhibits complex behavior beyond the chemist's paradigm of the pure chemical compound.

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P09 – Supramolecular chemistry of soot

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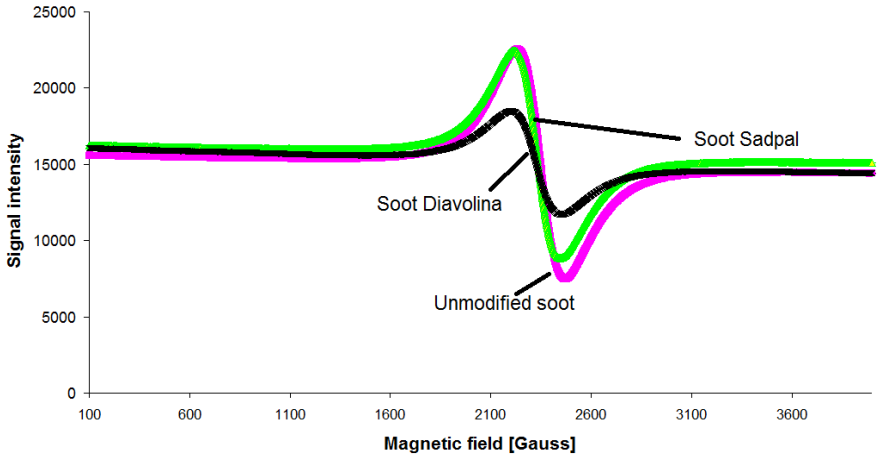
Soot contains fly ash, black carbon and carbonaceous matter. Carbonaceous matter has got very varied nature. There are carbonaceous forms like: carbon nanotubes, fullerenes (C_{60}, C_{70}), graphite, polycyclic aromatics (PAH), etc. PAH molecules are starting material in the formation of soot particles [1]. Soot has got very expanded area, and can serve as a good background for many chemical reactions. Supramolecular interaction between soot components as metal oxides (from fly ash) and volatile organic compounds provide condition for stabilization of radical state.

Some of soot components e.g. fullerenes are able to scavenging the free radicals [2]. However soot contains environmentally persistent free radicals (EPFRs) which are formed when an organic precursor chemisorbs onto a redox metal site (e.g., CuO or Fe_2O_3) subsequently reducing the metal via electron transfer [3]. A lot of reactive oxygen species (ROS) as well as EPFRs appear in the atmosphere, and they could promote cardiopulmonary dysfunctions.



EPR spectra of unmodified soot and modified soot samples

In our opinion fuel additives use in coal combustion are able to reduce unpaired electrons associated with soot. The additives reduce EPFRs level. That is why coal additives should be commonly used. Figure above shows a general tendency: fuel additives reduce the content of free radicals in the soot.

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P10 – Temperature Dependent On-Off Switching of Supramolecular Cage Formation Mediated by B←N Dative Bond

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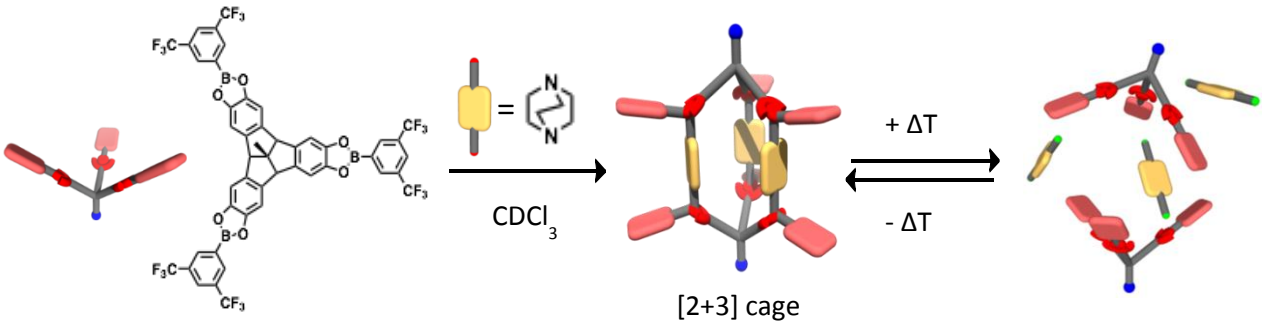
Over the last two decades, several attempts to mimic natural enzymes have resulted in a large number of self-assembled molecular cages based on various non-covalent interactions, e.g. hydrogen bonding, metal-ligand coordination or hydrophobic interaction.[1] Among them, boron nitrogen dative bond[2] is the least explored interaction to build molecular cages despite its unique properties such as facile tunability of its bond strength and its ability to construct neutral self-assembled molecular cages in contrast to charged metal-coordinated assemblies. Here we report on the synthesis of a soluble molecular cage utilizing boron-nitrogen dative bond formation.



[2+3] cage

The supramolecular cage was synthesized by reaction of a tribenzotriquinacene(TBTQ) tris-boronate ester and DABCO and characterized by ^{1}H-NMR and DOSY-NMR spectroscopy. Temperature dependent ^{1}H-NMR spectroscopy of the cage compound in *o*-dichlorobenzene solution revealed reversible switching between the molecular cage and individual building units.

References:

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P11 – Supramolecular control over LCST phase transition behaviors

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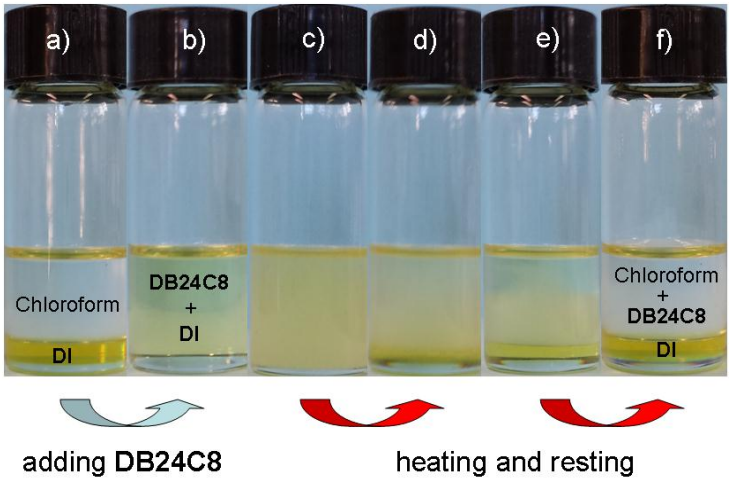
Supramolecular induced LCST-type phase changes were observed from a low molecular weight components system, in which neither of the components showed any thermo-responsiveness. In this thermo-responsive system, the supramolecular interactions between 1,3-dimethylimidazoliu iodide and dibenzo-24-crown-8 played a crucial role in yielding LCST-type phase separartions. The concentration, molar ratio of 1,3-dimethylimidazoliu iodide (DI) and dibenzo-24-crown-8, and the solvents, showed great influences on the properties of phase changes. These supramolecular induced LCST-type phase behaviors also presented interesting and unusual concentration-deperndent thermo-responsviebess, compared with conventional polymer-type LCST phase behaviors. Considering the controllability of supramolecular interactions and the diversity of supramolecular assemblies, this supramolecular induced LCST model system would serve as a platform to develop new LCST systems and to prepare thermally respensive materials.



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P12 – Imine and Imine-Analogue Compounds for Dynamic Covalent Chemistry

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Dynamic Covalent Chemistry (DCC) uses the reversibility of chemical reactions to build up thermodynamically controlled libraries.[1] For example, the reversibility of the reaction of amines with aldehydes or ketones allows the generation of dynamic covalent libraries (DCLs) of imines. By adding templates to these DCLs, members matching these templates can be amplified and the equilibria of the DCLs shift towards the matching products.[2]

An imine DCL is, for example, formed by the reaction of different oligo ethylene glycol diamines of varying lengths with a pyridine-dicarbaldehyde. Upon addition of alkaline earth ions, different diimines can be amplified (figure 1).[3]

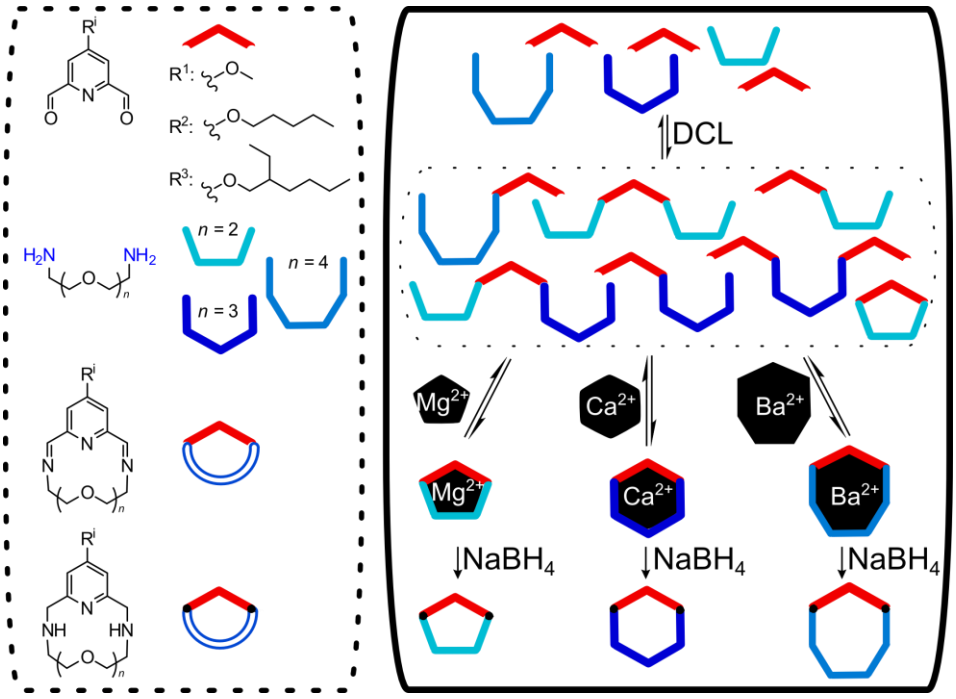

Figure 3: Schematic representation of possible members of the imine DCL formed by the reaction of different oligo ethylene glycol diamines with

Such a dynamic covalent imine library can be used directly for the selection of a carrier for transport.[4,5] First, template ions select hosts of matching size and amplify these. Matching macrocycles may possess different substituents R^i. In a second selection process, the membrane selects the best carrier.[2,4,5]

Oximes and hydrazones represent to imine-analogue compounds. They are generated by the reaction of hydroxylamines, or hydrazines and hydrazides with aldehydes or ketones. Combination of divalent building blocks leads to dynamic covalent libraries (DCLs) of oximes or hydrazones. Proper templates are investigated to shift the DCL towards matching products.

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P13 – Photo- and electrochemistry of redox-active interpenetrated coordination cages

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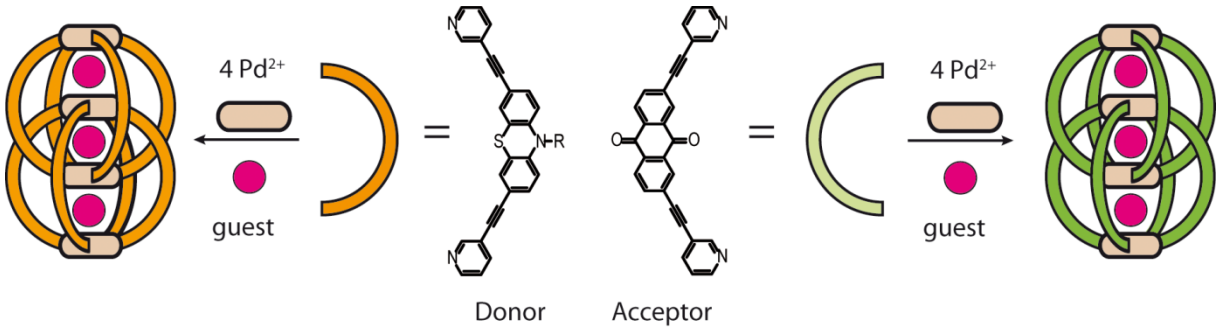
A direct synthesis of supramolecular, self-assembled coordination cages[1,2] starting from several building blocks offers a comfortable way to novel compounds with promising properties, such as selective recognition, storage, transport of guest molecules, etc.. Recently, we could show the synthesis and characterization of new coordination compounds based on the self-assembly of eight bispyridyl ligands with a phenothiazine backbone and four square-planar coordinated Pd(II)-ions.[3] The thermodynamically favoured product is an interpenetrated double cage.



Of particular interest are redoxactive compounds for electron transfer reactions. Combinations of electron rich phenothiazine and its derivatives with electron poor anthraquinone compounds are well established for applications in photoinducible electron transfer systems.[4] This system is known to undergo intramolecular photoinduced electron transfer, which results in the formation of charge-separated diradical ion pairs formed from singlet and triplet excited states. At present we are investigating this effect for these backbones incorporated in the double cage systems by applying time-resolved absorption spectroscopy and spectroelectrochemical methods.

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P14 – Multi-stimuli responsive supramolecular polymers

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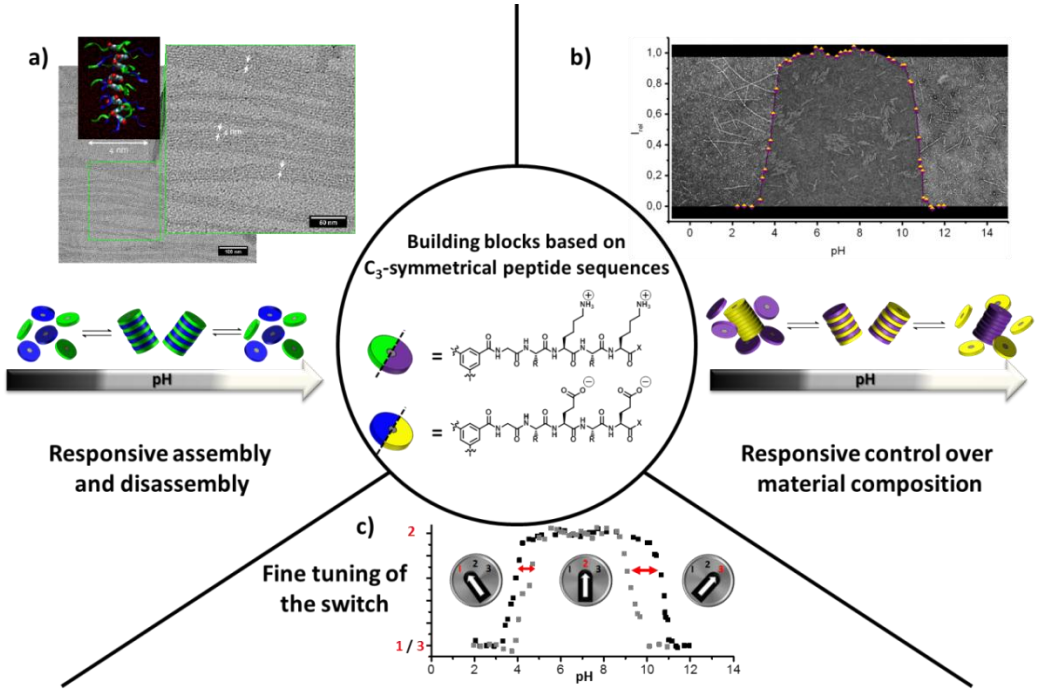
A particularly attractive feature of the non-covalent bond lies within its adaptive and responsive properties towards external stimuli.[1] We use these intriguing properties in order to design functional self-assembled materials, and have recently developed multicomponent systems consisting of two complementary peptide-based building blocks. These are able to function as supramolecular comonomers and initialise polymerisations into nanorodlike materials based on a number of non-covalent interactions in water. The ability of the building blocks to polymerise can thereby be switched on and off by the pH, in order to cause a controlled disassembly of the supramolecular copolymer into its comonomers (a).[2] Furthermore pH switching can be applied not only to control the reactivities of the supramolecular comonomers but also to control their selectivities in the supramolecular polymerisation. Thus, the polymerisation can be switched from copolymerisation to homopolymerisation of one of the comonomers and the simultaneous release of the complementary comonomer. Consequently this allows to control and alter the type of building block incorporated into the supramolecular polymer by an external stimulus (b).[3] The precise pH at which any of the switching processes is triggered can be adjusted by both a supramolecular engineering approach in the comonomer design, and by the chemical environment like the ionic strength and the temperature (c). Since the pH-switching process predominantly relies on protonating or deprotonating weakly acidic or basic functions incorporated into the comonomers, the controlled formation or disassembly of the polymers is reversible. This grants access to a unique class of multi-stimuli responsive multicomponent materials with great potential for biomedical applications.



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P15 – Chiral Porous Crystals for Enantiomeric Separation

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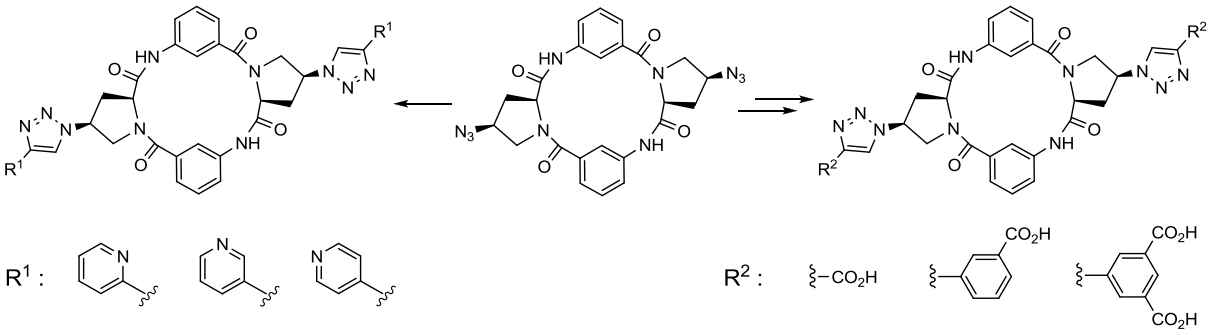
In about 230 million operations per year worldwide chiral, volatile anaesthetics such as isofluran and desfluran are used to maintain the anaesthesia during the surgery.[1,2] Since there are currently no efficient methods for their enantiomeric separation, these anaesthetics are administered as racemic mixtures. However, it is well known that two enantiomers of a drug can exhibit different pharmacological properties and one of them could also cause adverse side effects.[3,4] In the case of the above mentioned anaesthetics only one of them shows the desired effect.

The main goal of this research project, which is performed in collaboration with partners from Karlsruhe Institute of Technology and Université de Strasbourg, is to develop a chiral, porous and crystalline material that allows the enantiomeric separation of volatile anaesthetics by means of adsorption techniques. To this end, chiral stationary phases are developed comprising a three-dimensional coordination network composed of metal centers and organic ligands. As organic ligands, cyclopeptides with divergent coordination sites are used to introduce the chiral information into the network and to control its pore size.



My work concentrated so far on the use of a cyclic Tetrapeptide as central building block containing *L*-4-azidoproline and 3-aminobenzoic acid subunits. This precursor was converted into three structurally related cyclotetrapeptides, each of which contains two pyridyl moieties as Lewis-basic sites for coordination to the metal centers. In addition, the same precursor was converted into cyclopeptides containing at least two carboxylic acid residues, whose deprotonated forms could also serve to stabilize the coordination network. In this poster, the concept of this project and the synthetic approach are presented.

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P16 – Anti-cooperative self-assembly of a perylene bisimide dye into well-defined dimers by π-π-stacking and hydrogen bonding

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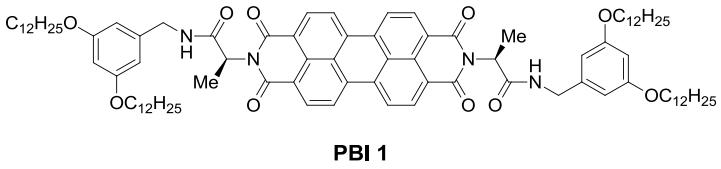
Perylene bisimide (PBI) dyes are known to self-assemble into one-dimensional aggregates, nano-fibers and columnar liquid crystals.[1] For systems where the self-assembly mechanism in solution has been explored, π-π-stacking has been found to follow the isodesmic model. If the π-π-stacking forces are supported by additional hydrogen-bonding units, the self-assembly can be enforced leading to cooperative growth into very long nanofibers.[2] Here we describe the very rare case of an anti-cooperative self-assembly of PBI dyes due to a very unique and strong self-assembly of PBI monomers into dimers.



PBI 1

*Figure 1: Structure of the homochiral **PBI 1**.*

We synthesized a novel homochiral **PBI 1** with peripheral solubilizing dialkoxybenzyl substituents bridged by L-alanine units. Self-assembly of the **PBI 1** in chloroform leads to π-stacked dimers with very high binding constant as confirmed by means of concentration-dependent ^{1}H-NMR and UV/Vis spectroscopic experiments. In contrast to the studies in chloroform, anti-cooperative growth via dimers toward larger aggregates could be observed in toluene which is attributed to the higher strength of both hydrogen bonding and π–π-stacking in this solvent.

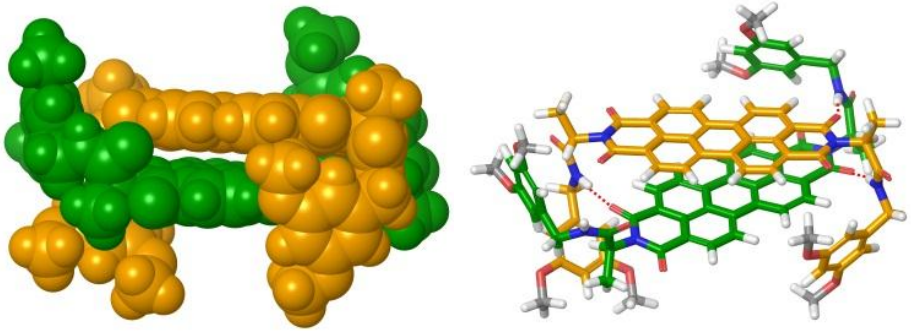


Figure 2: OPLS2001 geometry-optimized structure of the self-assembled PBI dimer.*

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P17 – Targeting Protein-Protein Interaction of 14-3-3 with c-Raf by Desing of Supramolecular Ligands

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The adapter proteins 14-3-3 have been shown to exhibit an extensive interactome with more than 200 partner proteins in human cells,[1] and more importantly, it was shown that 14-3-3 proteins are involved in many human diseases,[2] which makes this family an attractive therapeutic target for the treatment of a wide range of pathologies. In this regard, the design of supramolecular ligands which could recognize specific parts of the 14-3-3 protein surface will open the possibility of modulating those physiological functions in which 14-3-3 is involved throughout protein-protein interactions (PPI) recognition. In this work, we have focused on several surface-exposed aspartic and glutamic acids in the vicinity of the central binding channel of 14-3-3 where partner proteins like c-Raf or ExoS bind.[3],[4] Binding of a positively charged ligand to these negative residues should lead to the modulation (inhibition or stabilization) of 14-3-3 interactions with such partner proteins.

Recently in our group, we have performed a screening of several cationic ligands part of a home-made library in the search of 14-3-3 PPI modulators. Capillary electrophoresis (CE) experiments showed that two of these compounds stabilized c-Raf peptide 254-264 phosphorylated at Ser259 in its binding to 14-3-3ζ with EC_{50} values in the micromolar range. It is noteworthy that the GCP group, a home-designed cationic group that mimics an arginine side-chain,[5] showed to be a critical pharmacophoric feature in the peptide derivatives to its interaction with 14-3-3ζ. Therefore, and based on these validated hits, we have performed a screening of a new family of compounds built by means of a combinatorial dynamic synthetic strategy as modulators of the PPI interaction of 14-3-3ζ protein with its effector c-Raf. In all cases, the previous identified pharmacophoric element (GCP group) has been maintained.

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P18 – A New Approach to Substitute Cucurbiturils on the Methylene Bridge

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Cucurbiturils (CBs) are excellent host molecules in supramolecular chemistry with possible applications e.g. as receptors, sensors or catalysts.[1] The synthesis of substituted CBs is one of the greatest challenges in their chemistry. Substituents are needed to increase overall low solubility of CBs and to allow their further functionalization. Different attempts were used to introduce functionalities, e.g. post-synthesize modification[2] and cyclization of functionalized glycolurils.[3] The resulting CBs bear substituents on the convex face.

On this conference, the first example of a CB macrocycle with solely one substituent attached to the methylene bridge will be presented.[4] This compound was simply prepared by acid-catalyzed condensation of glycoluril and a mixture of paraformaldehyde and 3-phenylpropionaldehyde (Figure 1). The substituent affects supramolecular properties of the macrocycle. Furthermore, this approach is universal and can be translated for different aldehydes.

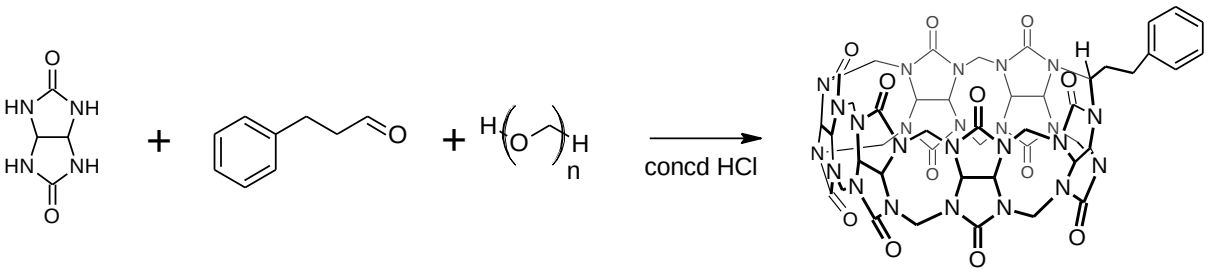

Figure 1

References:

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P19 – Synthesis and Characterization of a Novel C_3-Symmetrical Ligand in Supramolecular Chemistry

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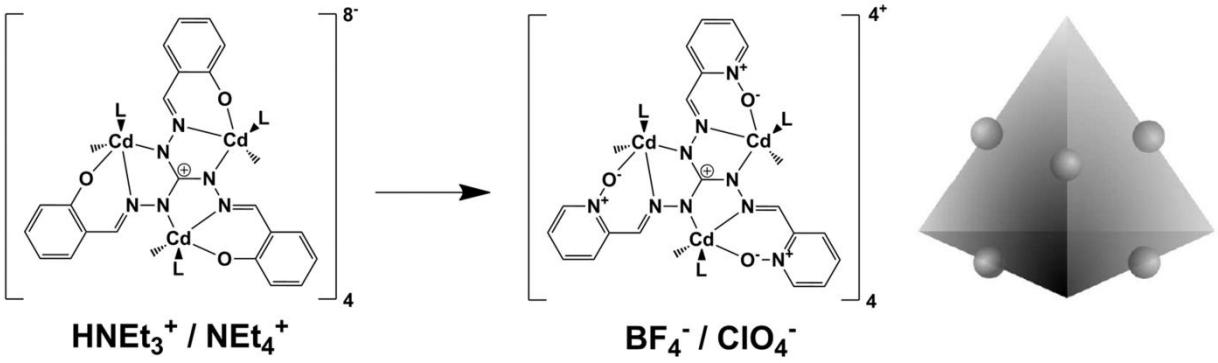
C_3-symmetrical triaminoguanidinium based ligands are able to coordinate soft metal ions like Zn(II)[1], Cd(II)[2] or Eu(III)[3] as well as hard metal ions like Ti(IV) or Zr(IV) in their tridentate chelating binding pockets. As the combination of ligands and metal ions provide flexible coordination environments, a variety of different discrete supramolecular coordination cages, such as tetrahedra[2], octahedra[4] and trigonal bipyramids[5], are accessible.

The work is focused on the synthesis and characterization of positively charged coordination compounds. This is achieved by the establishment of a new ligand type. The 2-pyridylene-N-oxide based ligand is able to chelate metal ions like the already literature known benzylidene-type ligands.[3] Additionally three positive charges are introduced to the ligand which allow the coordination complex to achieve an overall positive charge.



Possible applications of the tetrahedral structures could be the production of biodegradable polylactides, where the substrates polymerize in the presence of Lewis acids[6] and in the field of anion recognition.

On the poster we present the ligand synthesis, characterization and the first coordination compounds.

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P20 – Synthesis and self-assembly of octahydroxypyridine[4]arenes

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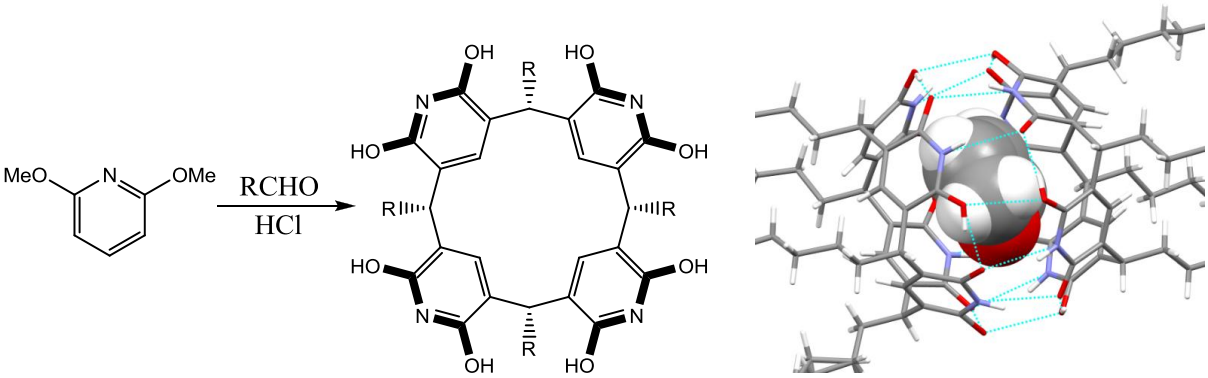
Octahydroxypyridine[4]arenes represent a relatively young class of members of the calixarene family and were first reported by Mattay et al. in 2001.[1] As shown in figure 1, these cyclic oligomers are obtained by acid catalyzed condensation of 2,6-dihydroxypyridine or 2,6-dimethoxypyridine with aldehydes.



They usually adopt a cone conformation, which is held together by a seam of intramolecular hydrogren-bonds between the functional groups of the wider rim. Furthermore, octahydroxypyridine[4]arenes show a distinctive self-assembly behavior as they readily form dimeric and hexameric capsules.[2] There are also distinct indications that they are capable of binding anions inside the dimeric container.[3] Our goal is it to synthesize rim-to-rim-connected octahydroxypyridine[4]arenes, to build up supramolecular polymeric structures held together by hydrogen-bonding and whose formation should be dependent of the chosen solvent.

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P21 – Reversed vesicles for the detection of organic compounds

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It is known, that amphiphilic surfactants form self-assembled micellar or vesicular structures.[1] Usually the term vesicle refers to spherical containers, which are formed in aqueous solution.[2] The outer shell of these vesicles is composed of a bilayer, while the vesicle core contains water. The counterpart to "normal" vesicles are reversed vesicles in organic solvents. They are build up by different kinds of amphiphiles, from which the hydrophobic part is exposed to the oily medium both in the core and in the exterior.[2] So far reversed vesicles have not been as intensively studied as "normal vesicles" and only few literature exists for their preparation[3]. Applications for this inverted vesicles are for example nanotemplating of plasmonically active SERS substrate and biocatalysis in reverse self-assembling structures[4]. For their preparation a literature known set up[2] was combined with the standard protocol, used in our group, for the establishment of normal vesicles[5]. Size and stability of the prepared inverted vesicles were determined by *Dynamic Light Scattering* to give reversed structures with 100 nm size and stability of around one week. For the detection of organic compounds a hydrophilic dye was embedded into the polar part of the bilayer, which was verified by fluorescence measurements. The recognition of organic substances should be monitored by changes of the emission properties of the dye.

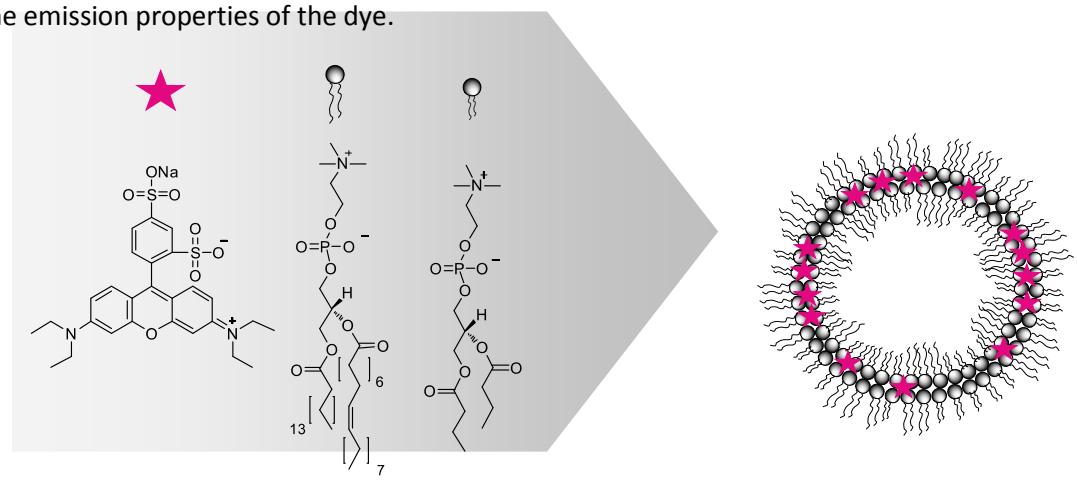

Figure 1: *Left: fluorescent dye sulforhodamine B, phospholipids L-α-phosphatidylcholine and 1,2-dibutyryl-sn-glycero-3-phosphocholine; right: reversed vesicle with dye embedded in the polar part of the bilayer.*

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P22 – Theoretical thermochemistry with wave function based (local) correlation methods: performance for sizeable and challenging supramolecular test cases

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The accurate prediction of thermodynamic properties is still a challenge for computational chemistry, at least if large molecules with significant long-range correlation are in the focus. Although dispersion corrected DFT methods are routinely applicable with good accuracy,[1] such approximate methods need to be benchmarked. Hence, a reliable reference method is desirable, particularly ifexperimental reference data are not accessible. One of the most promising candidates for this purpose is the recently published DLPNO-CCSD(T) method [2] although still more experience has to be gained for "real-lifeö chemical problems in order to finally judge on whether DLPNO-CCSD(T) can be used as general reference for thermodynamic properties of sizeable molecules as CCSD(T) is used for small systems. In particular, basis set related issues and the influence of the additional local approximations have to be under control. Based on a detailed performance assessment of DLPNO-CCSD(T) for association energies of large supramolecular complexes (S12L test set [3]) a standard protocol for accurate theoretical thermochemistry of larger molecules will be introduced.[6] Using this protocol, improved reference values for a challenging and important benchmark set (L7: interaction energies of large noncovalent complexes [4]) and further applications to large buckycatcher complexes [5] will be presented.[6]

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P23 – Coupled Molecular Switching Processes in Ordered Mono- and Multilayers of Stimuli-Responsive Rotaxanes on Gold Surfaces

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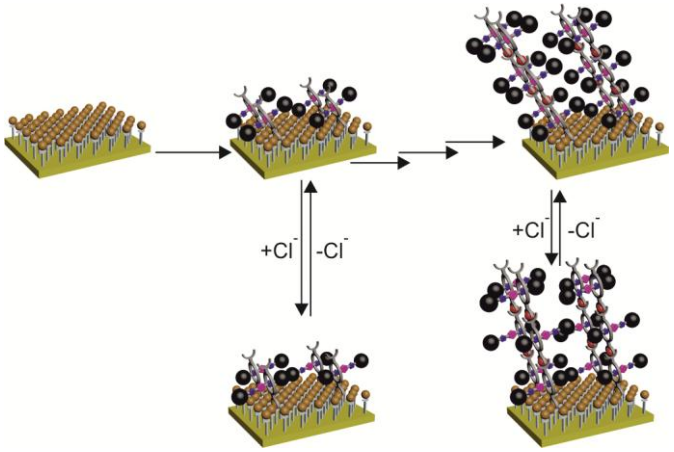
Interfaces provide the structural basis for function as, for example, encountered in nature in the membrane-embedded photosystem or in technology in solar cells. Synthetic functional multilayers of molecules cooperating in a coupled manner can be fabricated on surfaces through layer-by-layer self-assembly.



Ordered arrays of stimuli-responsive rotaxanes undergoing well-controlled axle shuttling are excellent candidates for coupled mechanical motion. Such stimuli-responsive surfaces may help integrating synthetic molecular machines in larger systems exhibiting even macroscopic effects or generating mechanical work from chemical energy through cooperative action. The present work demonstrates the successful deposition of ordered mono- and multilayers of chemically switchable rotaxanes on gold surfaces. For the first time, rotaxane mono- and multilayers are shown to reversibly switch in a coupled manner between two ordered states as revealed by linear dichroism effects in angle-resolved NEXAFS spectra. Such a concerted switching process is observed only when the surfaces are well packed, while less densely packed surfaces lacking lateral order do not exhibit such effects.

P24 – Fluorescent Liquid Crystal Based on Bay-substituted Perylene Bisimide

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In the growing field of organic electronic devices like as photovoltaics and organic field effect transistors perylene bisimides (PBIs) are currently among the most attractive class of organic dyes due to their potential broad range of applications.[1] Multiple hydrogen-bondings between free imide groups of PBIs as additional non-covalent interactions can lead to the formation of fluorescent J-aggregates.[2] Complex superstructures like liquid crystalls of PBIs with appropriate substituents at imide positions have already been reported.[3] But J-aggregating mesogenic PBIs bearing hydrogen atoms at imide positions have not been explored so far.

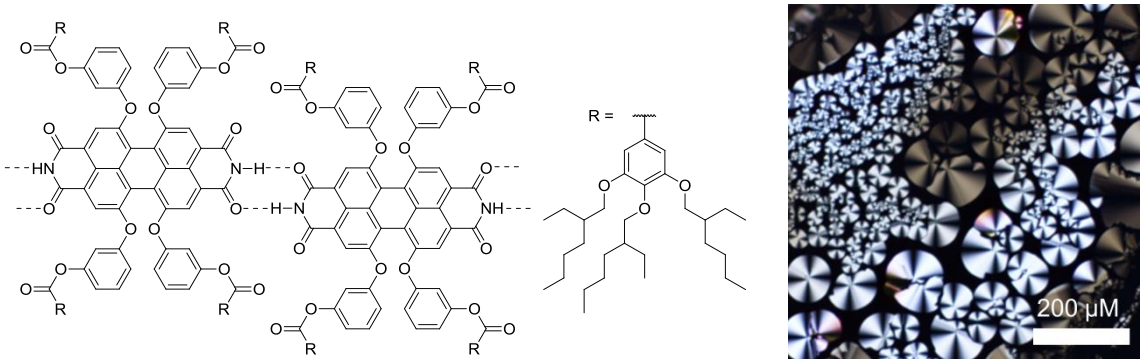

Figure: Self-Assembly of PBI dye by double hydrogen bonding motif (left). POM image of new PBI with typical pseudo-focal conic texture of a liquid crystal (right).

In our poster we present the synthesis and characterization of a new at core tetra-substituted perylene bisimide with free imide positions. The formation of slipped J-aggregates of this novel dye could be confirmed by concentration- and temperature-dependent UV/Vis studies. Investigations with temperature-dependent FT-IR measurements showed the reversible formation of hydrogen bondings between the imide groups. Our intensive investigations by POM, DSC and X-ray (SAXS/WAXS) revealed liquid crystallinity of this PBI and the formation of a new type of columnar arrangement in liquid crystalline packing motifs.

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P25 – New potentially allosteric receptors based on different bowl-shaped molecules

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In biological systems, there is a need for possibilities of regulating biochemical processes in order to prevent the system from over- or undersupplies. One concept to provide this control is based on allosteric effects. This term describes cooperative effects in the binding of more than one substrate to a single receptor where the binding of the first substrate- also called effector- causes a conformational change of the receptor resulting in an activating (activators) or deactivating (inhibitors) manner in terms of the binding of another substrate.[1,2]

Functionalized 2,2'-bipyridines fulfill all needs for acting as allosteric centers in artificial allosteric receptor-systems due to their ability to switch between *anti*- and *syn*-confomers upon coordination of transition metal ions.[3] In the past, we were able to synthesize many of those systems in which we used resorcin[4]arenes[4] or β-cyclodextrins[5] as substrates binding sites.

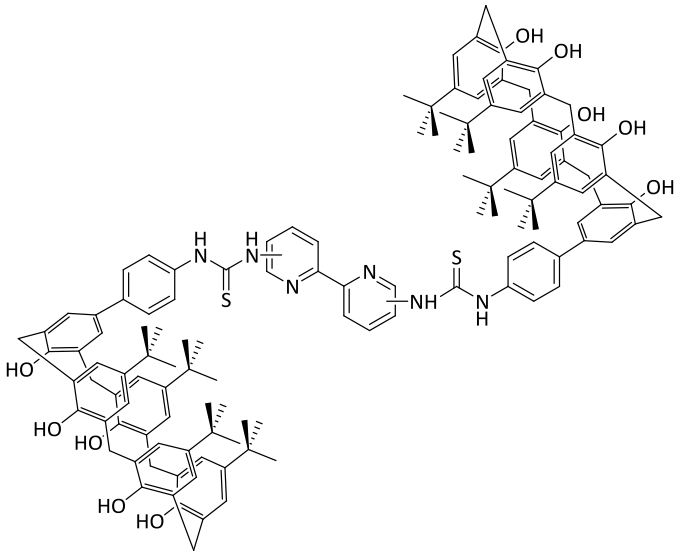

Fig.1: Allosteric system with calix[5]arenes

Searching for another type of bowl-shaped molecules we are now testing our allosteric 2,2'-byridines on calix[5]arenes[6](Fig.1) and octahydroxypyridine[4]arenes[7].

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P26 – A pH-switchable hydrogel from tripodal based trisZwitterion

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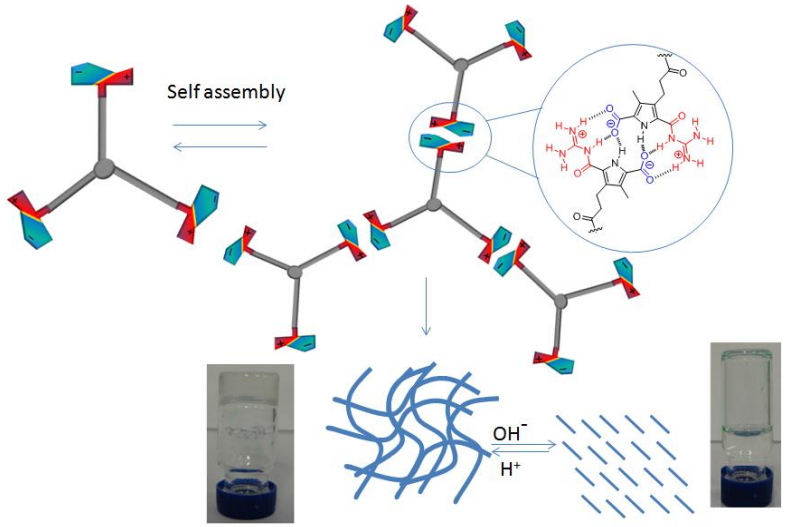
Stimuli-responsive gelation is highly interesting area of recent research due to their intriguing supramolecular architectures and potential applications in material chemistry and medicinal science.[1] The weak non-covalent interactions such as hydrogen bonding, π-π stacking, electrostatic and ven der Wall's interaction which are mainly responsible for the self-assembly process can be destroyed or rearranged by exposure to external stimuli. Different kinds of stimuli like pH change, solvent polarity, light, ultrasound, ions, enzymes, and so forth are usually used to tune the behavior of the molecular self-assembly for functional soft materials. In this context, we demonstrate a pH-switchable hydrogel formation from a tripodal based triszwitterion, the self assembly driven solely by the formation of ion-paired dimers between the self complementary zwitterionic units which form extremely strong dimers even in polar solvents ($K_{dim}>10^{10}M^{-1}$ in DMSO and $K_{dim}>10^{2}M^{-1}$ in pure water, respectively).[2]



Furthermore, the guanidiniocarbonyl pyrrole cation has pKa value of approximately 6–7, ion-pair formation with the carboxylate (pKa ~3–5) can occur only in a narrow and specific range around neutral pH. This provides a simple way of turning the aggregation on or off by either protonation or deprotonation of the zwitterion.

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P27 – Synthesis and Chiral Resolution of Functionalized Tröger's Base Derivatives and their Use in Metallosupramolecular Chemistry

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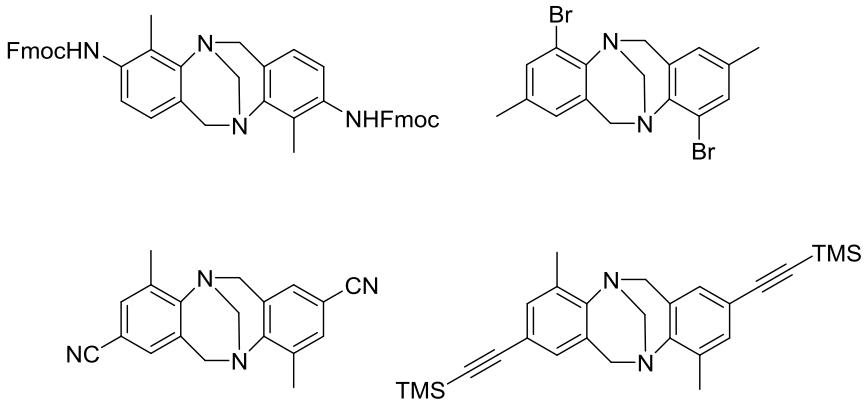
In the past our group was able to successfully resolve a large number of functionalized racemic Tröger's base derivatives.[1] Most of them contained halogen atoms for further functionalization. Now we are able to resolve a larger variety of functional groups in a semi-preperative or even preperative scale.



These compounds can either be directly used as ligands or easily be functionalized to amino, azido, cyano, or ethinyl Tröger's bases. They are valuable building blocks for the synthesis of more sophisticated ligand structures carrying nitriles, catechol, bipyridine, iminopyridine, pyridine, or phenanthroline units. These ligands are studied concerning their ability to form self-assembled metallosupramolecular aggregates.[2]

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P28 – Cavitands Incorporating a Lewis-Acidic Ni_2 Chelate Function as Receptors for small Anions

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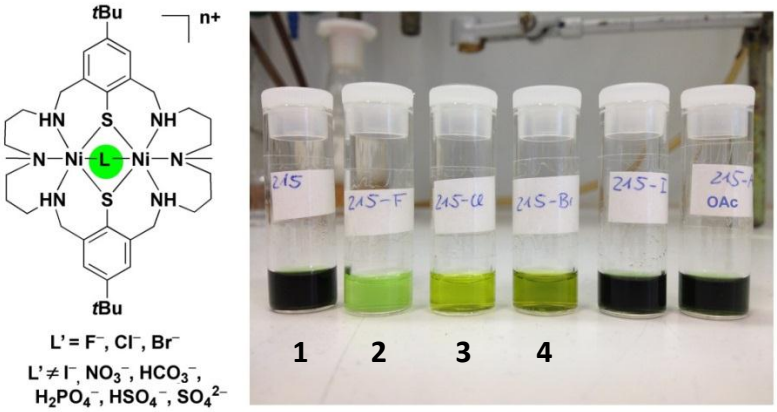
The synthesis, structure and anion binding properties of a new cavitand, namely $[Ni_2(L^{Me2H4})]^{2+}$ (**1**), are reported. The free receptor **1** is obtained by complexation of the hexa-hydrobromide salt of the partially *N*-methylated, macrocyclic N_6S_2 donor ligand H_2L^{Me2H4} with $NiBr_2$ in the presence of NEt_3.

Cavitand **1** exhibits a chelating $N_3Ni(\mu\text{-}S)_2NiN_3$ unit with two square-pyramidal $Ni^{II}N_3S_2$ units situated in an anion binding pocket of ~4 Å diameter formed by the organic backbone of the $(L^{Me2H4})^{2-}$ macrocycle. The receptor reacts with fluoride, chloride (in MeCN/MeOH), and bromide ions (in MeCN) to afford an isostructural series of halogenido-bridged complexes $[Ni_2(L^{Me2H4})(\mu\text{-Hal})]^+$ (Hal = F^- (**2**), Cl^- (**3**), and Br^- (**4**)) featuring a $N_3Ni(\mu\text{-}S)_2(\mu\text{-Hal})NiN_3$ core structure. No reactions occur with iodide or other polyatomic anions.

The binding events are accompanied by discrete UV–vis spectral changes, due to a switch of the coordination geometry from square-pyramidal (N_3S_2 donor set in **1**) to octahedral in the halogenido-bridged complexes (N_3S_2Hal donor environment in **2**–**4**). In MeCN/MeOH (1/1 v/v) the log K_{11} values for the 1:1 complexes are 7.77(9) (F^-), 4.06(7) (Cl^-), and 2.0(1) (Br^-).



X-ray crystallographic analyses for **1**$(ClO_4)_2$, **1**$(I)_2$, **2**(F), **3**(ClO_4), and **7**(Br) and computational studies reveal a significant increase of the intramolecular distance of two propylene groups at the cavity entrance upon going from F^- to I^- (for the DFT computed structure). In case of the receptor **1** and fluorido complex **2**, the corresponding distances are nearly identical. This indicates a high degree of pre-organization of the $[Ni_2(L^{Me2H4})]^{2+}$ receptor and a size fit mismatch of the receptors binding cavity for anions larger than F^-.

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P29 – Synthesis and application of fluorescent ligands for the self-assembly of metallosupramolecular aggregates based on BODIPY scaffolds

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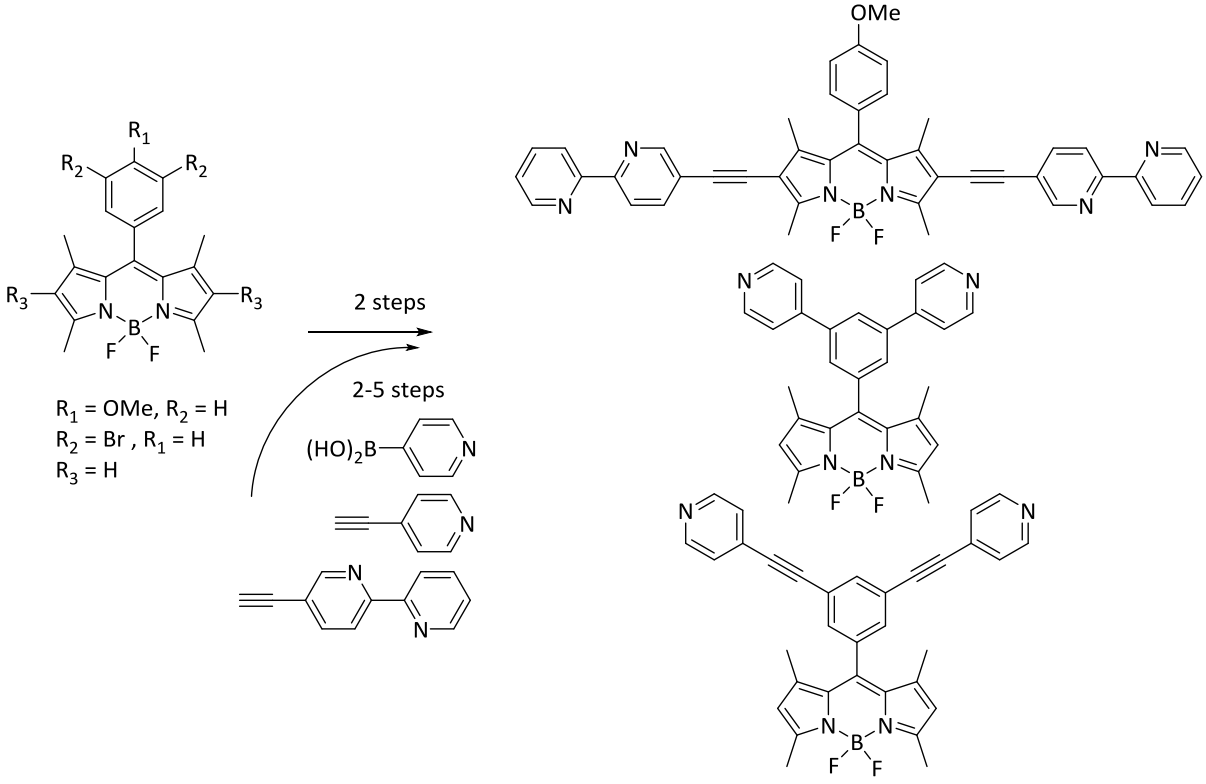
BODIPY (4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene) dyes have found a wide range of applications as versatile fluorophores.[1] A few years ago we began to use them as optical indicators for supramolecular processes in our group.[2,3] Even more recently, we decided to incorporate them into bidentate ligands such as bis(bipyridine)- or bis(pyridine) ligands and study their self-assembly to oligonuclear metalosupramolecular aggregates upon coordination to suitable transition metal ions. Here, we will present the synthesis of a first set of ligands that were designed to self-assemble into well-defined $M_{12}L_{24}$ or M_4L_6 aggregates.



The received aggregates should have interesting optical properties and in the future it might be possible to build aggregates whose host-guest chemistry might be easy to recognize due to the change of the aggregates fluorescent properties upon guest encapsulation. First NMR-, MS- and UV-VIS-data will be shown.

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P30 – Self-Assembly of Amphiphilic, Peptidic Au(I)-Phosphane Complexes into Luminescent Micelles in Water

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We present a facile synthetic route for the preparation of a new peptidic Au(I)-metalloamphiphile, using a nucleophilic water soluble Au(I) complex $H_2NCH_2C{\equiv}CAu^{I}$(TPPTS), and a NHS activated peptide Fmoc-Phe-Phe-NHS.[1] In buffered aqueous environments of medium to high ionic strength, Fmoc-Phe-Phe-$HNCH_2C{\equiv}CAu^{I}$(TPPTS) self-assembles into luminescent micellar nanostructures with an average diameter of 14 nm. In low ionic strength we have observed the formation of densely packed sheet-like morphologies. We expect that the luminescent properties can be assigned to electronic transitions from triplet-excited states due to the large STOKES and excited state life times, which are likely to be enhanced due to short Au(I)···Au(I) distances in the self-assembled nanostructures.[2] The facile synthetic strategy is fully compatible with peptide protecting group chemistry and allows for the construction of more complex peptidic nanomaterials in water, using our recently reported supramolecular synthons. By adjusting the hydrophilicity and charged character of tailor-made phosphane ligands bound to the metal complex, we aim to position functional Au(I) complexes into anisotropic nanostructures and exploit applications in bioimaging, catalysis and therapeutics.

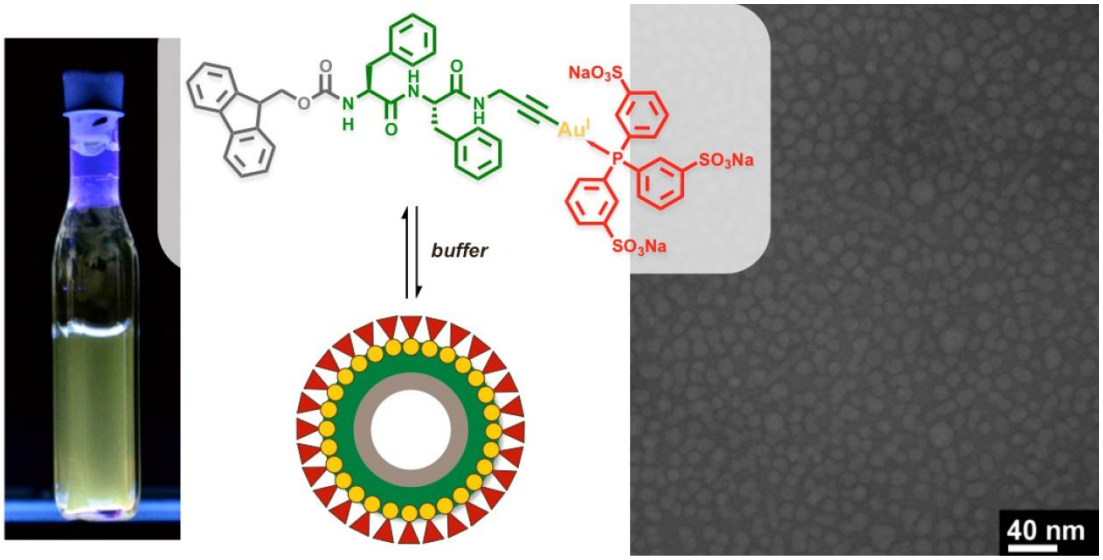

Figure 1: Luminescence (left) and morphology (right) of peptidic Au(I)-phosphane complexes, that self-assemble into micelles in aqueous buffered solution.[1]

References:

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P31 – Intramolecular Folding of a Bis(merocyanine) Tweezer

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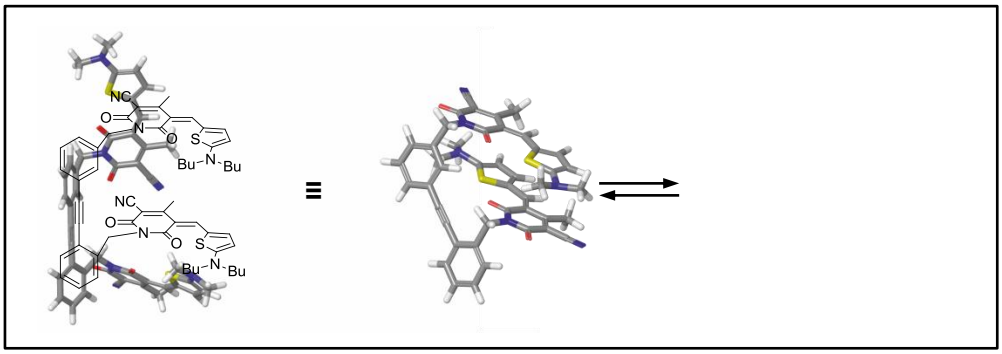
Merocyanines are a class of highly dipolar chromophores consisting of an electron-donating and an electron-accepting moiety. Owing to electrostatic dipole-dipole interactions these dyes self-assemble, particularly in nonpolar solvents, into dimers with antiparallel arrangement of their dipole moments.[1,2] In order to investigate the optical and electrochemical properties of merocyanine dye aggregates in solution, either highly dipolar compounds and high concentrations are needed or the stacking has to be supported by an appropriate covalent backbone.

In our poster contribution we will present the synthesis and characterization of a newly designed bis(merocyanine) dye in which two ATOP (AminoThienyl-OxyPyridone) chromophores are tethered by a rigid diphenylacetylene spacer unit. Our detailed investigation of this bis(merocyanine) by optical spectroscopy and one-dimensional as well as two-dimensional NMR techniques revealed that this compound undergoes an intramolecular folding process even in good solvating polar solvents. These unexpected but highly interesting results will be discussed in our poster.



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P32 – Metallosupramolecular helicates as model compounds for EPR-measurements

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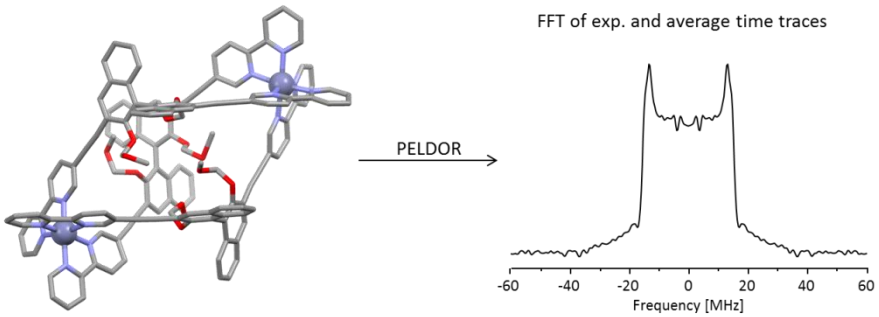
Metal ions are important building blocks in supramolecular chemistry, e.g. in helicates[1,2]. Especially iron(III)-ions are of importance in many biological processes and are key components of highly functional proteins, like e.g. hemoglobin or transferrin. Structural information about such systems are often available through X-ray crystal structure analyses[3,4] or NMR-spectroscopy. However, sometimes such systems do not crystallize, they are too large to be assessed by NMR and/or the metal centers are paramagnetic. Complementary to these methods a pulsed electron paramagnetic resonance (EPR) technique called pulsed electron-electron double resonance (PELDOR or DEER) has no size restriction, can be performed in solution and yields information about the structure and dynamics on the nanometer scale.



Here, we want to use PELDOR on the one hand to gain information about the structure and dynamics of helicates containing two or more paramagnetic Fe(III) or Cu(II) ions and on the other hand to get a deeper insight into multispin effects in PELDOR spectra. We have begun to prepare a number of $Fe(III)_2L_3$-helicates with different metal-metal distances. Simultaneous we use previously synthesized di- and trinuclear Cu(II)-helicates[5,6] as test compounds for the PELDOR approach.

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P33 – Chiral Porous Crystals for Enantiomeric Separation

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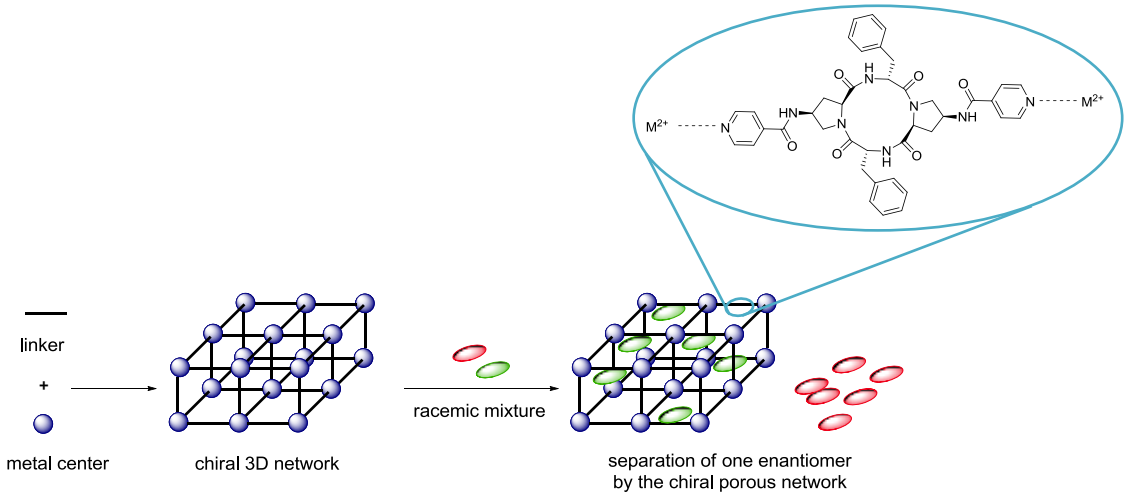
Worldwide over 230 Million major surgical procedures are performed every year and therefore anaesthetics hold a central role in surgery and the pharmaceutical market. [1] The anaesthetics that are used often contain chiral centres. Due to the lack of methods for efficient enantiomeric separation or enantioselective synthesis these narcotic gases are given as racemic mixtures even though only one enantiomer is narcotically active. In order to achieve the required narcotic effect the double amount of gas has therefore to be applied. As consequence side effects and longer times of convalescence can be observed since the unwanted enantiomer has to be removed from the body as well. At worst the other enantiomer could be harmful.



For that reason, developing a separation process for racemic mixtures of volatile narcotic gases is of importance. For the removal of the unwanted enantiomer physical separation techniques can be utilized. With a porous chiral material it should be possible to retard one enantiomer while the other passes through. Such porous network could consist of metal centers and organic linkers, the latter introduce chirality into the three dimensional system.

In this project cyclotetrapeptides, which are equipped with suitable Lewis-basic sites to enable coordination to a metal centre, are used as organic linkers for the construction of porous networks. The variation of the cyclotetrapeptide structure could allow optimization of the separation properties of the porous network with respect to the structure of a given anaesthetic. This research is carried out in collaboration with groups from Karlsruhe and Strasbourg with participation of the industrial partners. The work ranges from investigating the basic concept to the development of prototype materials, which can be used in practical applications.

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P34 – Design of artificial proteases for immobilization on Au-NPs as therapeutic option for amyloid diseases

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Neurodegenerative disorders such as Alzheimer's and Parkinson's diseases affect an increasing number of people in aging societies. In many of these diseases, protein misfolding and aggregation are involved. Therefore, the development of new methods detecting, understanding and preventing pathological protein aggregation processes are essential. In our approach, tailored nanoparticles are used as organizational platform and transport vehicle to combine different functional units. These are intended to cooperate synergistically in such a way that they perform peptide recognition, β-sheet breakage [1] and peptide cleavage.

To address this idea, we fabricated surfactant-free, monodisperse gold nanoparticles by laser ablation in saline solution [2] and conjugated different self-synthesized ligands.

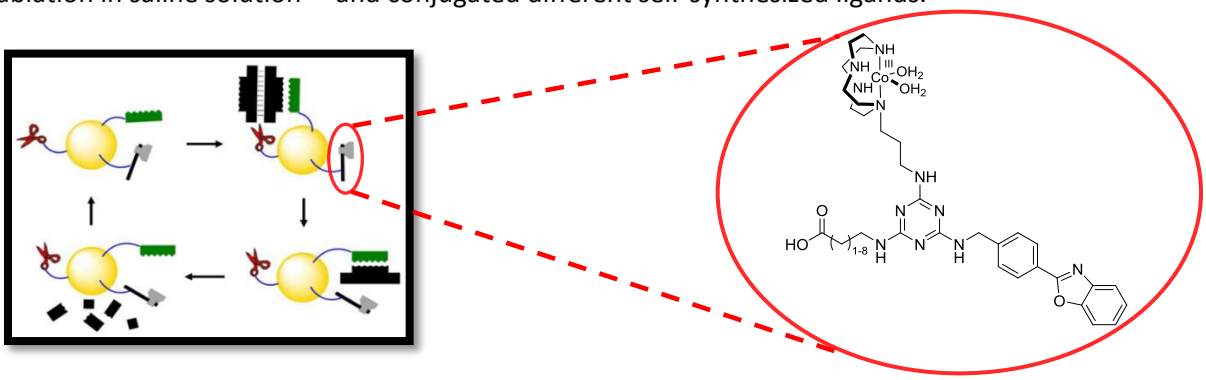

Figure 1. *left: Catalytic mechanism of trifunctional Au-NP construct. Green: recognition unit; red: β-sheet breaker; grey: protease; black: aggregating protein – right: Designed artificial proteases (Co-Cyclen-Complex)*

Here, we present the synthetic strategy for several potential artificial proteases for immobilization on gold. The underlying core structure has been published and was verified as cleaving agent for the peptide bond [3]. Cleavage activity was reported for $A\beta_{40}$, $A\beta_{42}$, h-IAPP and α-synuclein, which all form insoluble β-sheets. Optimization in our laboratory involves functionalization of side-chains with different anchor-groups and different C-spacer lengths.

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P35 – Embedding of a Ru(II) water oxidation catalyst into nanofibers via self-assembly

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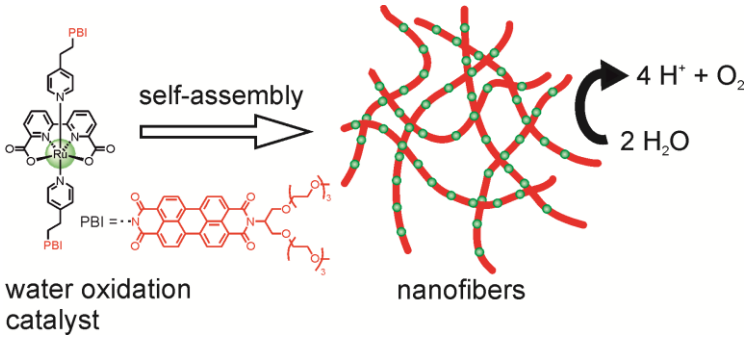
The splitting of water into its elements is an important approach for the generation of hydrogen as an alternative fuel. The bottle-neck of this process is considered to be the oxidative half reaction generating oxygen and good catalysts are required to handle the complicated redox chemistry involved.[1, 2] As can be learned from nature, the incorporation of the catalytically active species into an appropriate matrix can help to improve the overall performance.[3]



By the embedding of a ruthenium(II) water oxidation catalyst into supramolecular nanofibers higher catalytic turnover numbers and longer catalyst lifetimes have been achieved compared to a monomeric reference complex.[4] To construct these nanofibers, the catalyst was equipped with axial perylene bisimide ligands which facilitate the self-assembly due to strong π-π interactions.

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P36 – A tailor made specific anion binding motif in the side chain transforms a tetrapeptide into an efficient gene delivery vector

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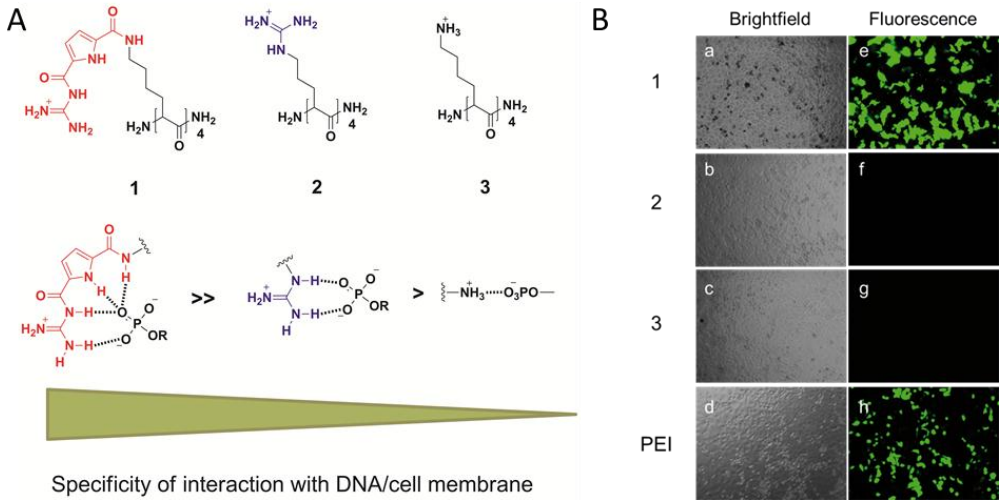
Arginine-rich cell penetrating peptides are widely utilized as gene delivery vectors. However, their transfection efficacy still needs to be optimized. Therefore, guanidinocarbonylpyrrole groups, a tailor-made anion binding site, were introduced in the side chains of tetralysine to obtain peptide analogue 1. In contrast to the common strategy of adding a lipophilic tail to peptide vector, this novel method shows an astonishing ability in enhancing transfection efficacy through the specific interactions between the binding motifs and DNA/cell membrane and thus resulted in the smallest peptidic transfection vector that has been reported so far. Such supramolecular binding motifs not only allow for more specific interactions with the DNA but also with the cell membrane. This enormously enhances the cellular uptake of corresponding peptide/DNA polyplexes relative to peptides with only natural amino acids. Transfection efficacy of 1, which on average has less than two positive charges under physiological condition, is even better than that of PEI. Furthermore, 1 exhibits only negligible cytotoxicity, which makes it an interesting candidate for further developments.



Scheme A. Oligopeptides 1-3 used for transfection studies. The GCP group in 1 is highlighted in red. In the order 1 >> 2 > 3 the specificity of the interaction between the cationic groups and oxoanions such as carboxylates or phopshpates decreases significantly. B. Transfection results with 2 µg pF143-GFP plasmid using 1, 2, 3 or PEI (all 0.15 mM).

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P37 – Encapsulation of Neutral Guest Molecules Inside Interpenetrated Coordination Cages

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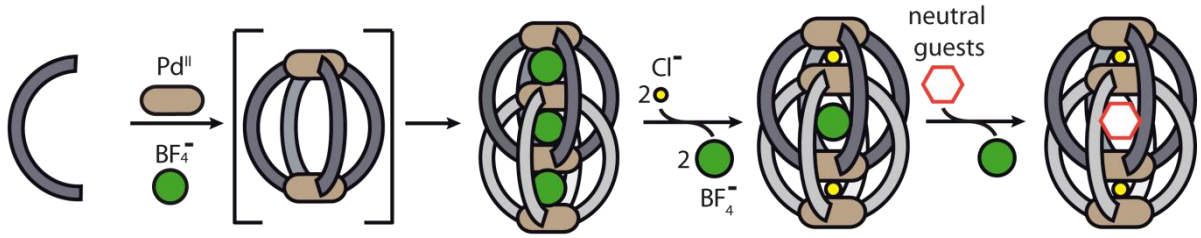
Supramolecular coordination cages have become a popular research area, due to their various usage. The cavity of self-assembled cages can serve as container for guest molecules or as environment for catalytic reactions similar to enzymatic processes. Interpenetrated double cages are of special interest, because they offer three mechanically coupled cavities, which are able to incorporate anionic guest molecules. [1]

Previously, we reported the formation of interpenetrated double cages [Pd_4L_8] based on dibenzosuberone and phenothiazine ligands.[2,3] Those structures are capable of allosteric anion binding with a tremendous affinity for the inclusion of two chloride anions in their outer pockets.[2,4]

Herein, we show that the formed, interpenetrated double cage based on a new acridone derived ligand also binds halide ions in its outer two pockets. Surprisingly, halide binding enables the double cage to encapsulate neutral guest molecules, such as benzene, cyclohexane or norbornadien in its central pocket. Currently, we are studying the application of this halide-triggered binding mechanism in the context of double-input receptors, molecular logic gates and switchable catalysis inside confined cavities.



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P38– Kinetico-Mechanistic Insights on the Assembling Dynamics of Allyl-Cornered Metallacycles

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The square-like homo- and heterometallamacrocyles $[\{Pd(\eta^3\text{-}2\text{-}Me\text{-}C_3H_4)(L^n)_2\}_2\{M(dppp)\}_2](CF_3SO_3)_6$ (dppe = 1,3-bis(diphenylphosphino)propane) and $[\{Pd(\eta^3\text{-}2\text{-}Me\text{-}C_3H_4)(L^1)_2\}_2\{M(PPh_3)_2\}_2](CF_3SO_3)_6$ [py = pyridine, M = Pd, Pt, L^n = 4-PPh_2py (L^1), 4-$C_6F_4PPh_2$py (L^2)] containing allyl corners were synthesized by antisymbiotic self assembly of the different palladium and platinum metallic corners and the ambidentate N,P-ligands. All the synthesized assemblies displayed a complex dynamic behavior in solution, which is found to be dependent on the electronic and/or steric nature of the different building blocks as was studied by time-dependent NMR-Spectroscopy in combination with Electrospray mass spectrometry (ESI-MS).

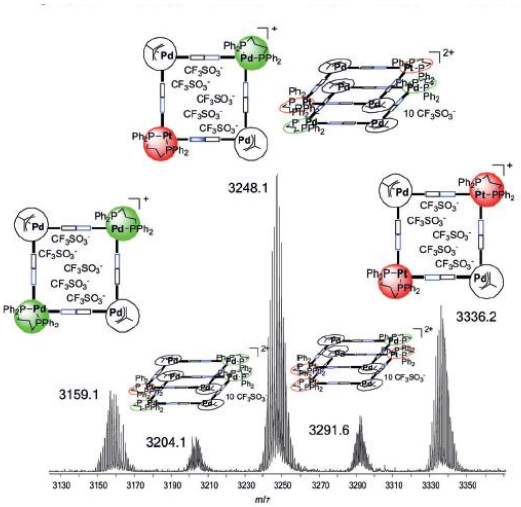

Figure 1: ESI-MS spectrum of a 1:1 Mixture of $[\{Pd(\eta^3\text{-}2\text{-}Me\text{-}C_3H_4)(L^1)_2\}_2\{Pd(dppp)\}_2](CF_3SO_3)_6$ and $[\{Pd(\eta^3\text{-}2\text{-}Me\text{-}C_3H_4)(L^1)_2\}_2\{Pt(dppp)\}_2](CF_3SO_3)_6$ after equilibrium is reached.

ESI-MS is a soft ionization method that has been widely applied for the characterization of supramolecules. For this study a series of ESI -experiments with equimolare mixtures of respectively two metallacycles in acetone were carried out after determined time intervals until equilibrium was reached. The results show slower kinetics of Pt-N_{Py} versus Pd-N_{Py} bond, despite its increased lability on the fully assembled metallamacrocycle.

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P39 – Selective Ratiometric Detection of Heparin in Plasma Using a Molecular Peptide Beacon

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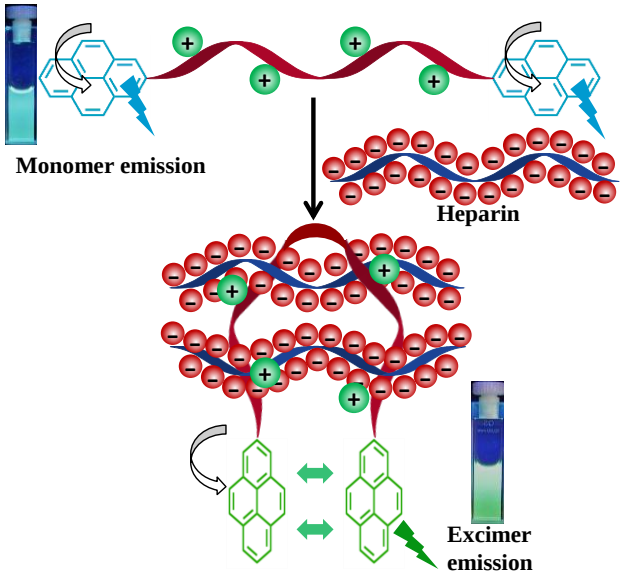
Heparin is a highly sulfated glycosaminoglycan having a high negative charge density. It is used as effective anticoagulant to prevent thrombosis during surgery and to treat thrombotic diseases.[1] However, heparin overdose can cause adverse effects such as hemorrhages, thrombocytopenia and hyperkalemia.[2] Therefore, it is necessary to monitor and quantify the level and activity of heparin during and after surgery to avoid heparin-overdose induced complications.[3] A novel molecular peptide beacon has been developed for selective ratiometric detection of heparin in aqueous media



based on pyrene monomer-excimer mechanism. The lysine rich cationic peptide is capable of binding the negatively charged heparin. Complex formation is reflected in changes in the pyrene fluorescence properties due to the concomitant formation of pyrene monomer-excimer. This peptide could monitor heparin ratiometrically at nanomolar level in diluted bovine serum. DLS and AFM studies also confirm aggregate formation of heparin with peptide. Moreover, this method is highly selective for heparin relative to other similar biological analytes.

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P40 – Dynamic Covalent Functionalization of Liposomes

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In nature, many recognition processes take place on cell surfaces. Therefore it is crucial to transfer the results from solution experiments to membranes. It was shown that benzylic thioesters can reversibly bind to thiols, achieving rapid equilibration in dynamic combinatorial libraries (DCLs) under physiological conditions.[1] Using this strategy, we recently investigated the functionalization of liposomes via thiol-thioester exchange.[2] We now applied this principle of covalent, dynamic chemistry to decorate liposomes with thiolated carbohydrate derivatives, creating a model glycocalyx (Figure 1).

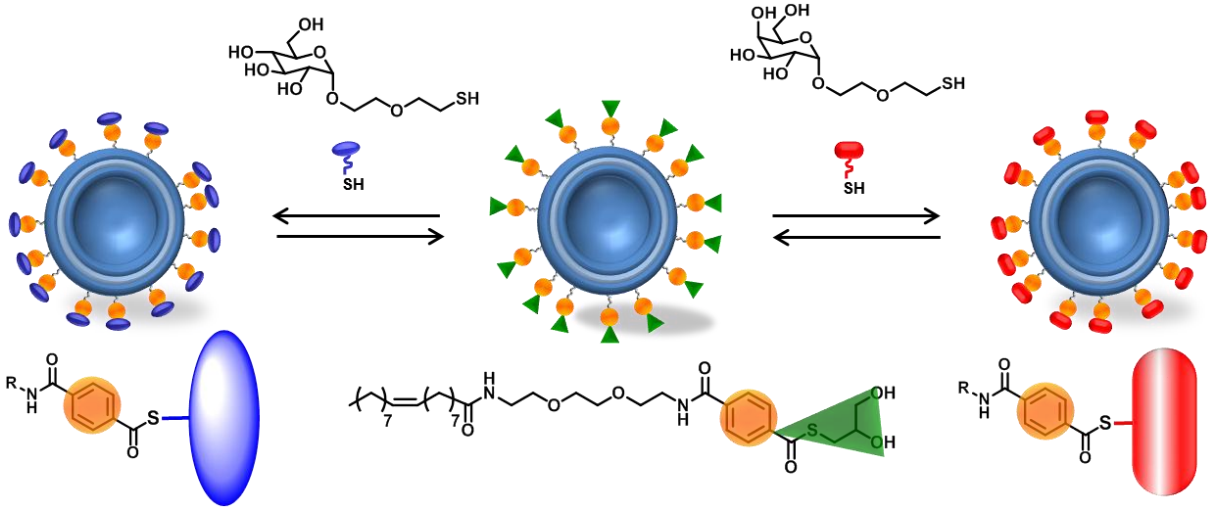

Figure 4: Dynamic functionalization of liposomes with carbohydrates via thiol-thioester exchange.

Future focus will lie on exploring this systems capacity to simulate carbohydrate recognition by lectins. To this end we will examine the dynamic self-optimization of the functionalized membrane surfaces via a DCL approach.

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P41 – Synthesis and Anion Binding Properties of a Macrocyclic Pseudohexapeptide Containing 1,4-Disubstituted 1,2,3-Triazole Subunits

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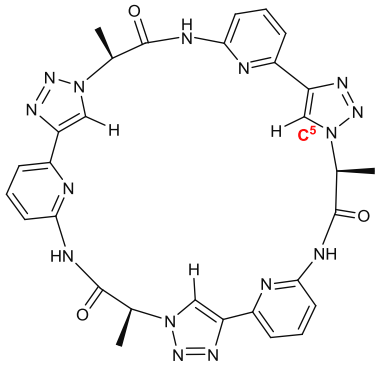
Recognition of anions has gained attention in the field of Supramolecular Chemistry due to the vital role of anions in the environment, in biology and in industry.[1, 2] Although a large number of anion receptors has been developed so far, designing selective hosts is a challenge due to the intrinsic properties of anions that render them relatively difficult substrates.[2] The importance of anion recognition motivated us to design the new receptor 1 comprising a cyclic pseudohexapeptide.



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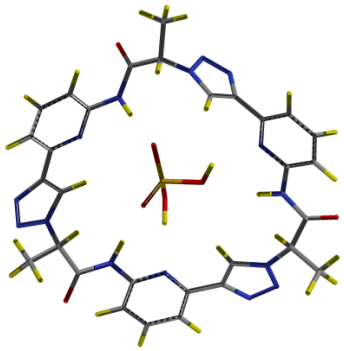

Calculated structure of the complex of 1 with a $H_2PO_4^-$ anion

Receptor 1, containing N-(pyridin-2-yl)propanamide and 1,4-disubstituted 1,2,3-triazole subunits, was synthesized by using a combination of peptide and click chemisty. It was expected that its interaction with anions would involve the NH groups along the ring in combination with the C^5-H groups of the triazole subunits. NOESY NMR indicated that all potential hydrogen bond donors of 1 are indeed oriented in a converging fashion thus creating an electron deficient binding site for anions. Preliminary binding studies of 1 with various anions (chloride, bromide, iodide, hydrogen sulfate, nitrate and dihydrogenphosphate) showed that all of these anion bind to 1 in DMSO-d_6/acetone-d_6, 1:20 (*v/v*). In my contribution I will present the synthetic strategy used to prepare 1, the conformational investigations and the results of ^{1}H-NMR titration experiments.

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P42 – pH-Responsive Single-Chain Polymer Nanoparticles based on Guanidinocarbonyl Pyrrole Carboxylate Zwitterion

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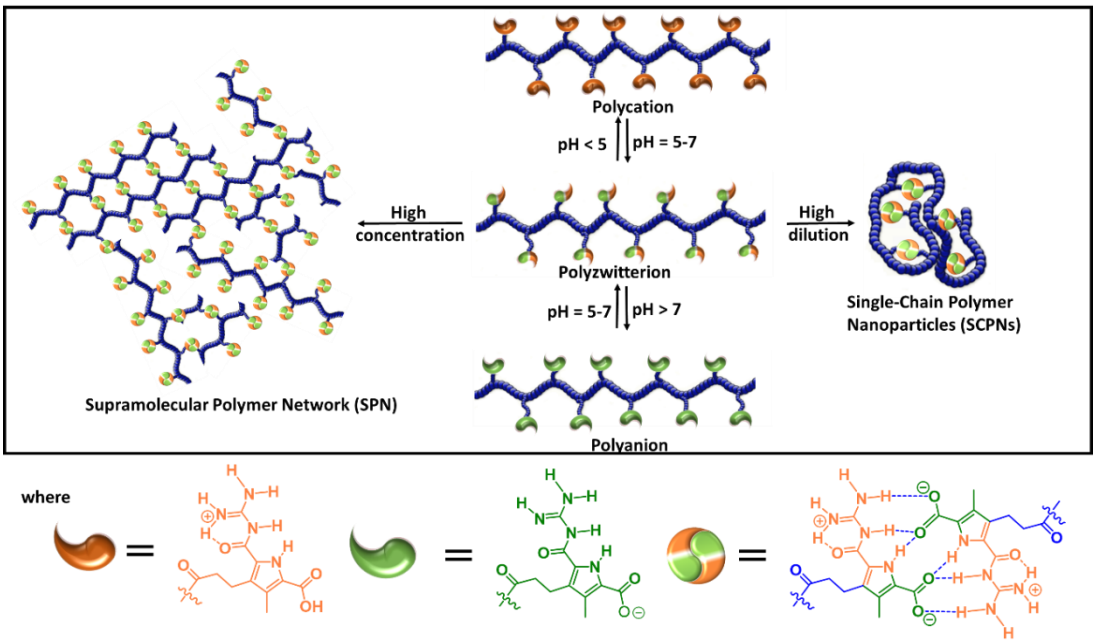
The field of SCPNs recently experienced substantial development and such materials are envisioned as promising nanocarriers for applications in biomedicine.[1] The concept of folding or collapsing of individual polymer chains into small nanoparticles through intramolecular non-covalent interactions has emerged as an efficient alternative synthesis of well-defined smart functional materials such as nanoparticles.[2] We report the synthesis of zwitterionic pH-responsive polymer nanoparticles based on the self-dimerization propensity of the guanidinocarbonyl pyrrole (GCP) carboxylate zwitterion.[3] Polystyrene substituted with GCP carboxylate zwitterions in the main chain forms a supramolecular



polymer network (SPN) at higher concentration. However, dilution resulted in the formation of single-chain polymer nanoparticles (SCPNs). The formation of both the supramolecular polymer networks and the single-chain polymer nanoparticles are evidenced by Dynamic Light Scattering (DLS) and Atomic Force Microscopic (AFM) analyses. Stimuli-responsiveness of the supramolecular polymer network and SCPNs has also been demonstrated by DLS and AFM analyses.

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P43 – Boronic Acid Functionalized Peptides as Carbohydrate Receptor

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Carbohydrate recognition plays an important role in various biological processes like cell-cell recognition, inflammation and infections of cells by viruses and bacteria. Embedded in cell membranes in form of glycoproteins and glycolipids, carbohydrates take part in protein-carbohydrate interactions at the cell surface.[1] To understand these processes the development of synthetic carbohydrate receptors is crucial.

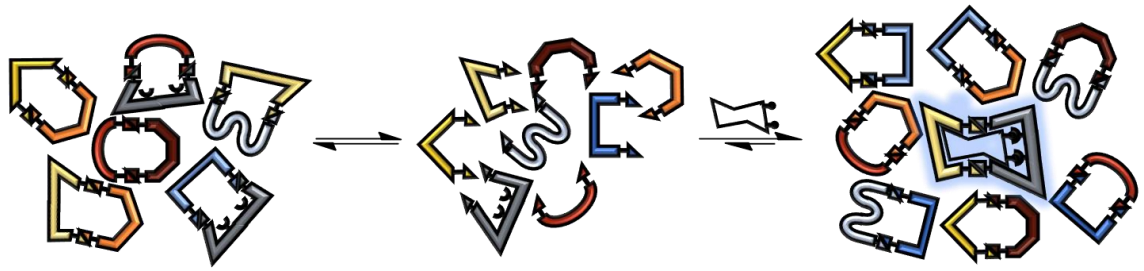

Figure 5: Schematic illustration of a Dynamic Combinatorial Library, which contains natural and boronic acid functionalized peptides with the motif Cys-X-Cys.

Since a long time it is known that phenylboronic acids have a high affinity to bind diols.[2] This property makes phenylboronic acids an interesting structural element for the field of carbohydrate recognition. We report the synthesis of boronic acid functionalized tripeptides with a Cys-X-Cys motif (X = phenyl boronic acid functionalized amino acid). These peptides can work as carbohydrate receptors by themselves. Moreover, they can be used in dynamic combinatorial libraries (DCL's) to find more potent receptors (Figure 1).

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P44 – Responsive Soft Materials by Self-assembly

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Self-assembly is emerging as a superior method to prepare adaptive and responsive nanomaterials. Responsive multivalent interactions are key to such versatile materials. This lecture will highlight soft material composed of cyclodextrins and/or superparamagnetic nanoparticles. It will be shown that using the host-guest chemistry of cyclodextrins, we can form hydrogels as well as nanocapsules. We can also make “magnetic vesicles” that self-assemble in microscale linear aggregates in aqueous solution under the influence of a magnetic field. The metastable linear aggregates can be stabilized by a noncovalent and photoresponsive cross-linker, which can be photoisomerized between an adhesive and a nonadhesive configuration. Thus, the hybrid material responds to magnetic field as well as to light and a stable self-assembled structure can only be obtained in a magnetic field in the presence of the noncovalent cross-linker. We have recently extended this strategy to superparamagnetic nanoparticles modified with cyclodextrin. These hybrid nanoparticles can be further functionalized using host guest interaction and molecular recognition and they can be used to capture and isolate proteins.

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P45 – Spirobifluorene-based dyes for supramolecular self-assembly systems

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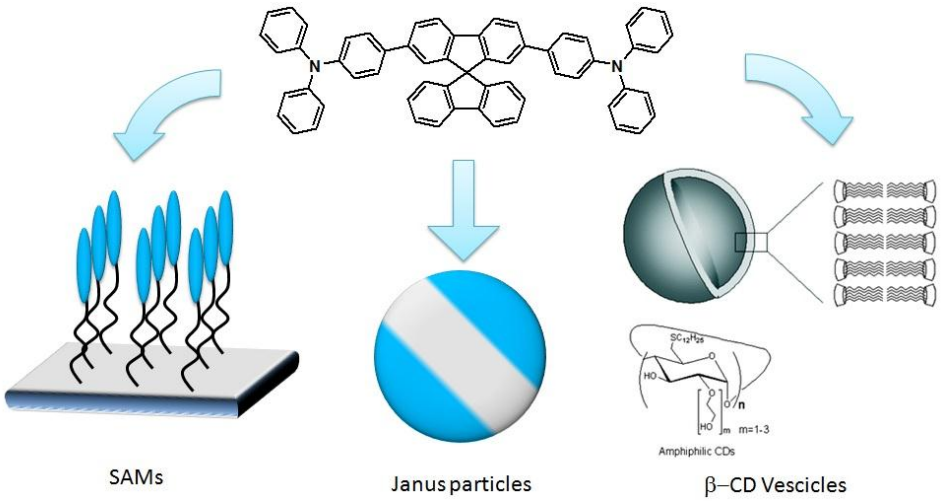
In the past years, spirobifluorene-based molecules have been applied in different technological fields due to its chemical versatility. In particular, the spirobifluorene bearing two triphenylamine moieties in position 2 and 7 (see Figure) shown interesting luminescence properties in the field of non-linear optics[1] and electrochemiluminescence[2]. Until now this class of dyes was investigated at molecular level, i.e. in solution, or as layer in devices like organic light emitting diodes[3]. However, studies focused on supramolecular systems using spirobifluorene derivatives as emitting species are completely missed.



In this communication we want to show preliminary results about the use of this dye in supramolecular systems. In particular, by introducing specific binding site, we were able to form monolayers on solid substrates or to obtain blue emitting Janus particles by using self-assembly process. Moreover, the combination of the spirobifluorene dye with cyclodextrin vescicles results in a system suitable to investigate photoelectron transfer phenomenon which will be also reported.

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P46 – Molecular Self-Assembly of 1:1 Mixtures of Tetracationic Guanidiniocarbonyl Pyrrole and Na_4EDTA: Formation of Small Molecules to Supramolecular Polymer through Intermolecular cationic/anionic Interaction in $DMSO/H_2O$

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Molecular self-assembly is a process in which molecules spontaneously form ordered aggregates without guidance or management from an outside source. The weak noncovalent interactions such as hydrogen bonding, π-π stacking, electrostatic and van der wall's interaction play important role for the self-assembly process can be destroyed or rearranged by exposure to external stimuli. In this context, we have developed an electrostatic and hydrogen bond[1,2] inducing molecular self-assembly process in polar solvent when 1:1 mixtures of tetra cationic guanidiniocarbonyl pyrrole and Na_4EDTA have been used (Figure 1). The two low molecular weight monomers form supramolecular polymer and size of the polymer seems to be increasing in solution depending on time which was exposed by infrared laser-based dynamic light scattering (DLS), and atomic force microscopy. The association of two monomers

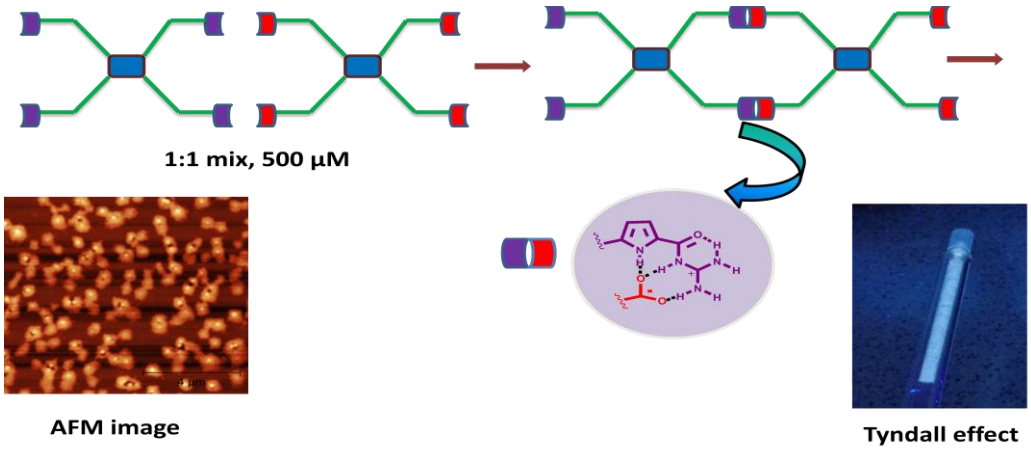

Figure 1: (1:1) mixtures of tetracationic guanidiniocarbonyl pyrrole and Na_4EDTA

and the formation of polymer were established by NMR titration, fluorescence measurement and viscosity experiment. At high concentration (5-6 mM), a stable colloidal solution was formed which showing nice Tyndall effect at room temperature. However, the strong Tyndall effect indicates the larger aggregates in concentrated solutions.

We are going to present the synthesis and detailed results on my poster.

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P47 – Influence of Host Guest Interactions on the Fluorescence of Spirobifluorenes

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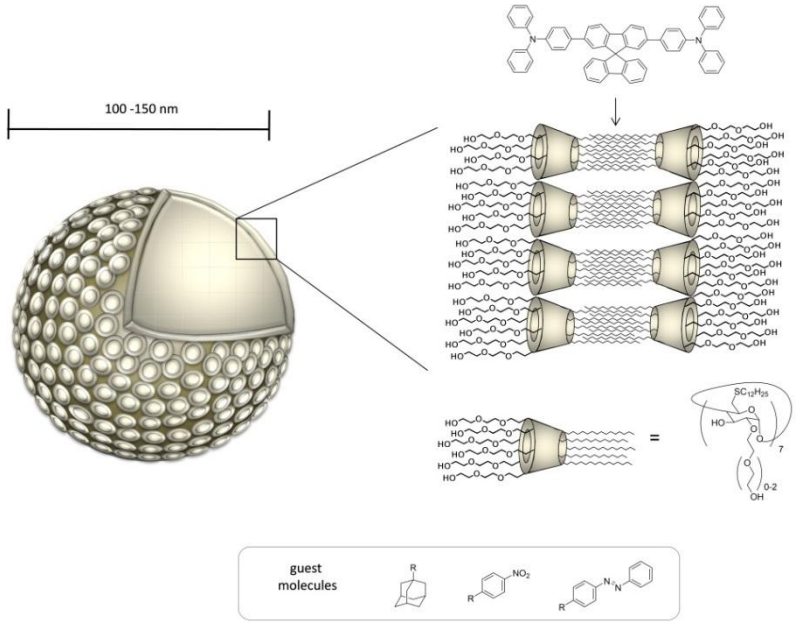
Vesicles are widely used as model compounds for biological membranes. They are able to encapsulate water-soluble molecules in the aqueous interior and hydrophobic molecules into the bilayer membrane. Synthetic amphiphilic vesicles can additionally consist of a binding motive and selectively bind complementary molecules. For example amphiphilic cyclodextrin vesicles can form selective inclusion complexes at the surface of the vesicle.[1]

Here we report the encapsulation of 2,7-bis-(4-(*N,N*-dipenylamino)phen-1-yl)-9,9'-spirobifluorene, a high emmisive dye[2], into the membrane of β-cyclodextrin vesicles to establish a luminescent chemosensor in aqueous solution. Selective binding of guest molecules directs the quenching molecule to the dye and should thus lead to effective quenching of fluorescence. The encapsulation of the dye was verified by fluorescence measurements and fluorescence microscope images of giant unilammelar vesicles (GUV). We investigated various nitrobenzene and azobenzene derivatives as quenching guest molecules and compared the results of β-cyclodextrin vesicles to α- and γ-cyclodextrin vesicles as well as phospholipid liposomes without binding motive. Moreover, we investigated reversible quenching due to isomerization of azobenzene. The processes were analyzed by fluorescence, absorption, dynamic light scattering and fluorescence lifetime measurements.



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P48 – Boronic acid probes in supramolecular analytical chemistry

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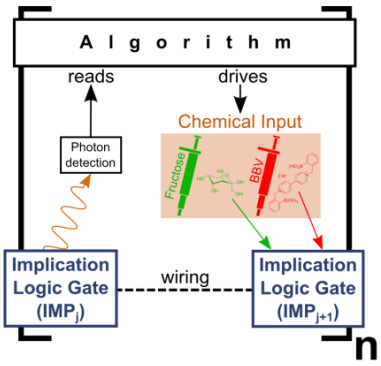
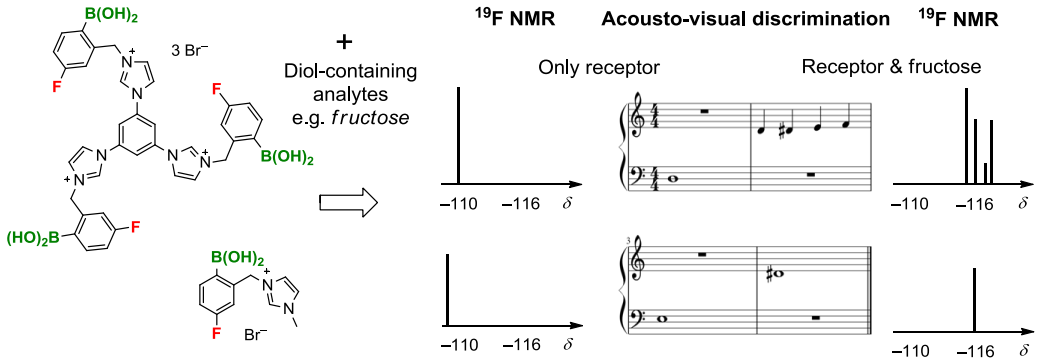
Indicator displacement assays (IDAs) represent an elegant approach in supramolecular analytical chemistry.[1] We use boronic acid appended viologens together with fluorescent dyes in allosteric indicator displacement assays (AIDA) to detect sugars at physiological conditions.[2-4] The AIDA probes describe the molecular logic function implication (IMP). Binary switching was monitored on the few-molecule level of the reporting dye.[5] A "sugar computer" was generated on microtiter plates. Logic circuits have been constructed by using the functional completeness of the IMP function. An external wiring algorithm translates the fluorescent output into a chemical input for the next gate. This has been demonstrated on a four-bit full adder for number crunching[6] and on playing tic-tac-toe.[7]



However, the intrinsically unselective flourescent signal can be exchanged by highly sensitive ^{19}F NMR detection. Fluorinated boronic acid pyridinium and imidazolium salts have been used to discriminate diol-containing analytes at aqueous conditions. The binding event was measured via ^{19}F NMR shift; discrimination was enabled with two-dimensional barcodes.[8] The complexity of the signals increases with multitopic receptors. Finally, the signals can be converted into musical notes for acousto-visual discrimination.



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P49 – Development of Cyclic Peptides Containing 4-(1*H*)Pyridone Subunits

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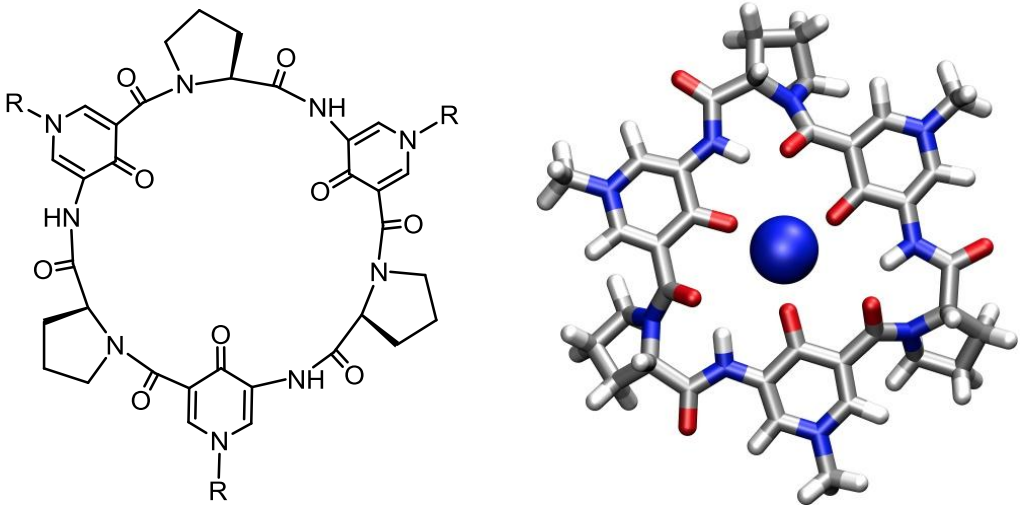
Cyclopeptides are attractive scaffold for the development of macrocyclic synthetic receptors. They are synthetically relatively easily accessible and available in a structurally wide range by the exchange of individual building blocks.[1] In addition, even in the absence of other functional groups they contain the built-in NH-groups and the C=O-groups of the peptide units that can be used for the binding of anionic or cationic guest molecules.[2]

A strategy to broaden the scope of potential guests and the efficiency of binding involves introduction of non-natural subunits into the cyclopeptide ring. In this respect, a range of different macrocyclic receptors have been developed in the Kubik group containing an alternating sequence of natural and aromatic amino acids. A new member of this family of receptors is the cyclopeptide shown below that contains L-proline and 4-(1*H*)pyridone-derived subunits. This peptide is expected to interact with alkali metal ions due to the converging arrangement of carbonyl groups as shown in the calculated structure of its potassium complex.



For the preparation of this peptide, appropriately functionalized 3,5-disubstituted 4-(1*H*)pyridone derivatives are required. These building blocks can then serve to prepare the repeating dipeptide subunits along the ring, which in turn should allow the preparation of the corresponding macrocycle. In my poster, I will present my synthetic work toward the preparation of the 4-(1*H*)pyridone-containing cyclopeptide.

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P50 – Cyclic Peptides for Secondary Structure Elucidation

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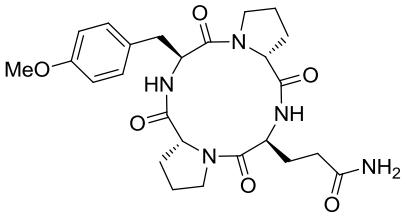
Cyclic Peptides are an important and versatile class of natural products with many of them exhibiting high biological activities. In many cases, this activity is related to the ability of cyclopeptides or analogous natural macrocyclic products to interact with charged substrates such as inorganic cations or anions. Prototypical examples are cyclosporin or the cyclodepsipeptide valinomycin. As there is a strong correlation between binding affinity and the overall conformation of a cyclopeptide, investigations addressing the influence of individual amino acid subunits along a cyclopeptide ring on its conformational behavior are crucial to derive structure activity relationships.



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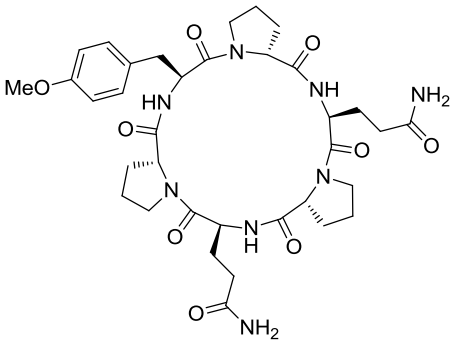

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In this respect, the mass selective IR/UV spectroscopic studies in the gas phase combined with DFT calculations performed in the group of M. Gerhards in Kaiserslautern are potent tools to elucidate the structure of isolated molecules, including cyclopeptides, and their adducts with neutral (water) or charged species. These investigations eventually lead to a better understanding of the structural aspects that control the interaction of a peptide with an ion.

After initial investigations on relatively hydrophobic cyclopeptides,[1] current work focuses on cyclopeptides with polar side chains such as the cyclic tetrapeptide *cyclo*[L-Gln-D-Pro-L-Tyr(OMe)-D-Pro] (1) and the corresponding cyclic hexapeptide *cyclo*[(L-Gln-D-Pro-L-Gln-D-Pro-L-Tyr(OMe)-D-Pro] (2). The glutamine subunits in these compounds are expected to induce affinity for alkali metal ions such as sodium or potassium ions. In my poster, synthetic studies aimed at preparing cyclopeptides 1 and 2 are presented.

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P51 – Near-IR Phosphorescent Ruthenium(II) and Iridium(III) Perylene Bisimide Metal Complexes

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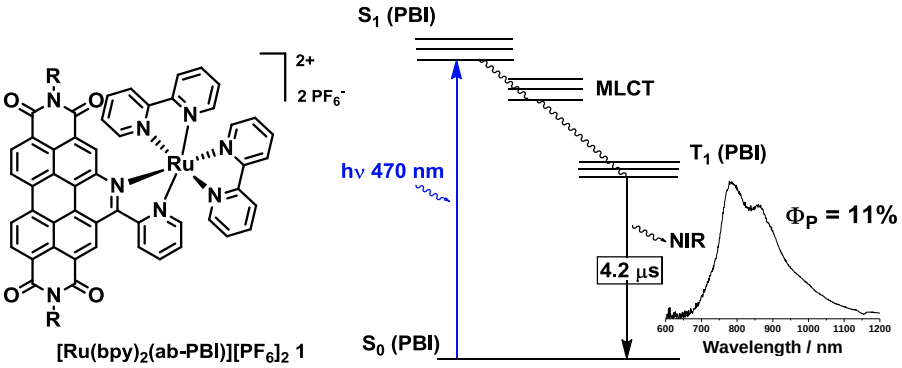
In the progress to increase the longevity of utilizable excited states (*e.g.* charge separated and triplet states) many donor/acceptor dyads and triads were developed in the recent decades.[1] In this regard, perylene bisimides (PBI) arouse certain interest as electron acceptors due to their excellent photostability and strong photooxidative power.[2] So far there are only few examples of PBI-metal adducts reported and in these the influence of the metal leads to different photophysical phenomena like charge separation, PBI triplet state generation or unchanged PBI emission (despite heavy metal).[3] Especially, phosphorescence emission of perylene bisimide of PBI-based transition metal complexes has not been reported in literature so far.

In this context, we present two novel ruthenium(II) and iridium(III) complexes of an azabenz-annulated perylene bisimide (ab-PBI), $[Ru(bpy)_2(ab\text{-}PBI)][PF_6]_2$ and $[Cp^*Ir(ab\text{-}PBI)Cl]PF_6$, both showing NIR phosphorescence between 750 – 1000 nm in solution at room temperature.[4] The ruthenium complex displays for NIR emitters an unusually high quantum yield (Φ_p) of 11% with a lifetime (τ_p) of 4.2 µs, while the iridium complex exhibits Φ_p < 1% and τ_p = 33 µs. The two compounds are the first PBI-metal complexes in which the spin-orbit coupling is strong enough to facilitate not only the $S_n \rightarrow T_n$ intersystem crossing of the PBI dye, but also the radiative $T_1 \rightarrow S_0$ transition, *i.e.* phosphorescence.



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P52 – Synthesis of achiral and chiral anilinosquaraines and their application in optoelectronic devices

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Anilinosquaraines represent one of the most often studied class of squaraine dyes and some derivatives like 2,4-Bis[4-(*N,N*-diisobutylamino)-2,6-dihydroxyphenyl]squaraine have even become commercially available.[1,2] This class of small-molecule chromophores combines many advantages like easy synthesis with high purities, high thermal as well as photostability, and outstanding absorption properties. Here, we present some of our results in synthesis and application of these dyes. In solid state squaraines tend to form H- and J-aggregates. This supramolecular arrangement can most notably be influenced by varying the substituents at the amine terminus. The incorporation of longer or branched alkyl chains also leads to superior solubility in organic solvents and facilitates solution processing. However, chiral derivatives are scarce and have received relatively little attention so far.[3,4] Chirality is a promising additional structure-defining motif and may lead to interesting absorption characteristics (i.e. sensitivity to circular polarized light). We utilize two possible concepts in our efforts to synthesize chiral squaraines: either we start from enantiomerically pure educts (e.g. proline derivatives) or we prepare the compounds as racemic mixtures which are subsequently resolved via chiral HPLC.

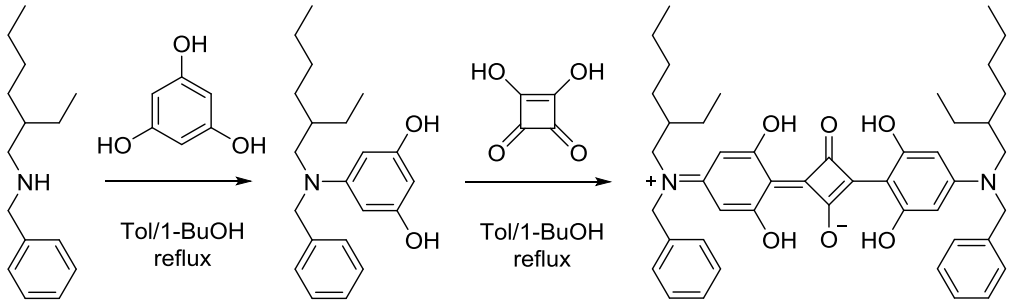

Figure 6: Synthesis of squaraines with chiral alkyl substituents.

Cooperation with the University of Oldenburg Institute of Physics enables us to incorporate our squaraines in solution processed optoelectronic devices (i.e. bulk-heterojunction solar cells).[5,6] The engineering, characterization, and optimization of these devices is another interesting field of research and some data will be presented.

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P53 – Photoswitchable Rotaxanes for Deposition in ordered Multilayers on Gold Surfaces

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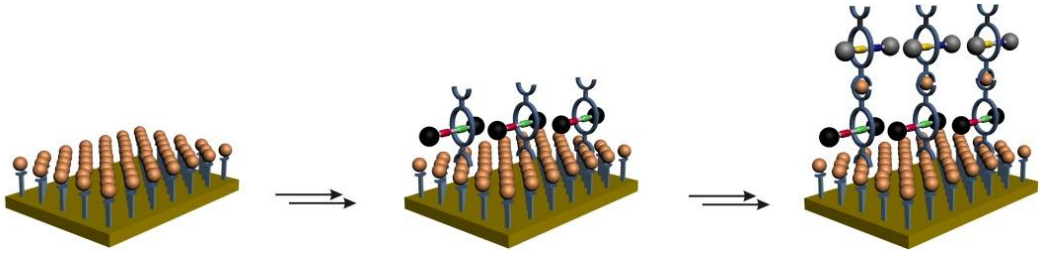
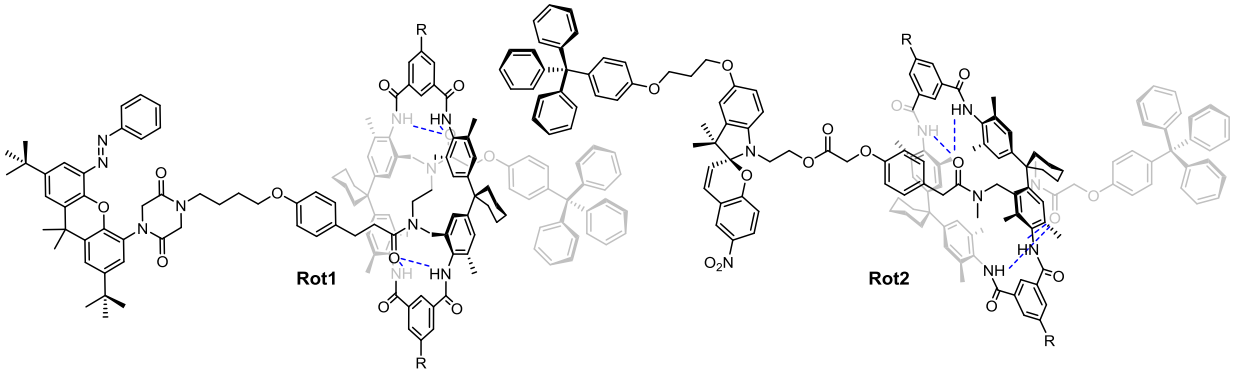
Stimuli responsive chemical systems capable of performing molecular motion are of great interest for the development of functional materials and molecular machines. Immobilizing such molecules on surfaces allows the concerted action of molecular switches and shuttles. Multilayers of different supramolecules can be deposited on gold surfaces via layer-by-layer self-assembly using metal-ion pyridine/terpyridine complex chemistry. [1]



The integration of photoswitchable rotaxanes into these systems enables orthogonal stimulation of different rotaxane layers as well as advanced analytical possibilities for surface characterization. Novel photoswitchable rotaxanes capable of reversible switching between two distinct states by external light stimuli have been synthesized and characterized. Using azobenzene and spiropyran as photoactive units, two systems with different photophysical properties are available.



In **Rot1**, the position of the azo group influences the binding strength of the adjacent diketopiperazine binding station via steric hindrance, while the open form of the spiropyran in **Rot2** acts as a binding station itself.

References:

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P54 – Investigation of Structural Mimetics of Natural Phosphate Ion Binding Motifs

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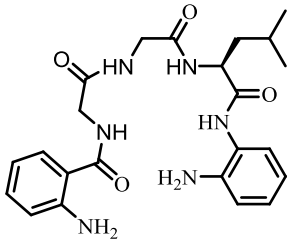
Phosphates play an important role in biology and many proteins interact with their partners with the help of phosphate residues [1, 2].The predominant part of proteins includes a so-called “P loop”, which is essential for the affinity for the phosphate residue. It contains glycine-rich sequence with several other amino acids. To the best of our knowledge, there is no precedent in the literature with the investigation of anion binding properties of model compounds containing several glycine residues in the recognition motif. Thus, in this work two new receptors 1 and 2 have been designed and synthesized and their anion binding properties in acetonitrile solution have been determined.



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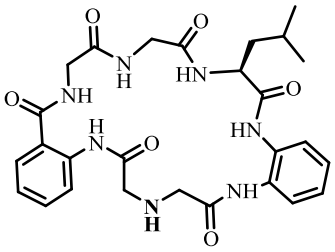

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These new receptors repeat the glycine-rich “P loop” containing the sequence GGL. This sequence was functionalized from both ends with aromatic compounds with the aim to rigidify the overall structure of the receptors and to allow the investigation of binding constants with the help of UV-Vis and fluorescence methods. The amino groups were introduced as hydrogen-bond-acceptor groups to facilitate the coordination of anions bearing protons, such as dihydrogen phosphate and hydrogen sulfate. According to spectrophotometric measurements, stepwise 1:1 and 1:2 binding modes have been observed for both receptors in the presence of acetate, hydrogen sulfate and dihydrogen phosphate. Compared with the acyclic receptor 1, the macrocyclic receptor 2 has demonstrated a remarkably enhanced selectivity for dihydrogen phosphate over other anions. Fluorometric measurements have revealed different responses of the acyclic and macrocyclic receptors towards anions. Binding constants obtained from fluorescence measurements were in a good agreement with those obtained by UV-Vis titrations.

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P55 – Visible Light Triggered Azobenzene Photoswitch for Cyclodextrin-Based Supramolecular Systems

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Azobenzenes are the most used photochemical switch due to their excellent photophysical properties, their easy synthesis and modification possibilities.[1] A lot of work has been done to develop azobenzenes which could be triggered with light of the visible or the IR region to expand their application to biological fields.[2] Additionally, the formation of light responsive host-guest inclusion complexes of azobenzenes and cyclodextrins (CDs) is well known. While the rod-like *trans*-isomer forms a stable inclusion complex with α- and β-CD the more polar and bent *cis*-isomer does not fit in either CD cavity.[3]

In this work we report on the synthesis of an *ortho*-fluorinated divalent azobenzene moiety which is suitable for cyclodextrin-based supramolecular systems. Furthermore, a separation of the n→π*-band is observed in the UV/vis absorption spectrum, so isomerization can be triggered by irradiation with visible light (520 nm and 455 nm) in a selective manner. By UV/vis spectroscopy excellent switching behaviour of this compound was found. The reversible formation of host-guest inclusion complexes with β-CD, β-CD vesicles and β-CD decorated nanoparticles was investigated by optical density (OD 600), dynamic light scattering (DLS) and isothermal titration calorimetry (ITC) measurements (Figure 7).

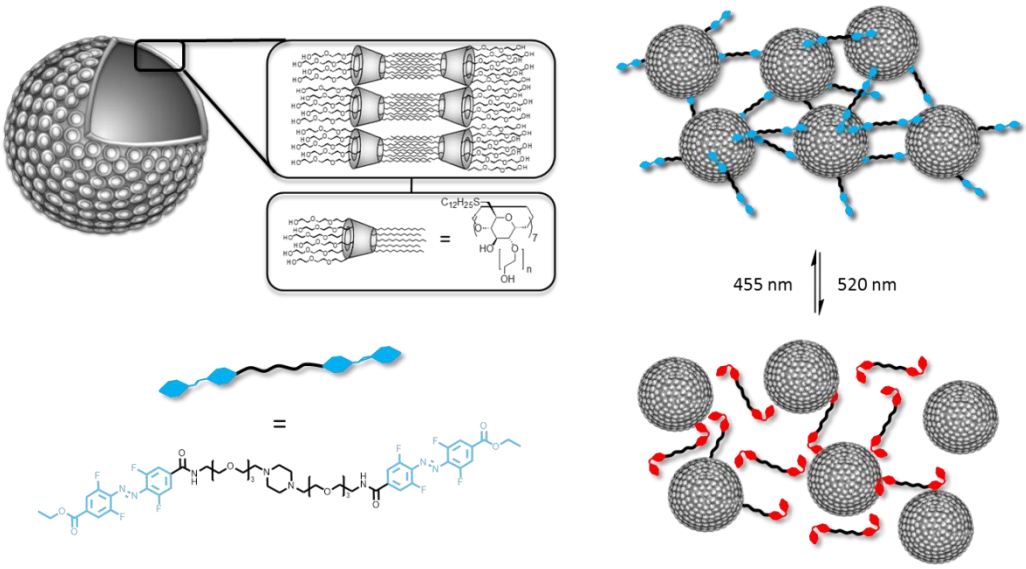

Figure 7: Structures of CD vesicles and the synthesized *ortho*-fluorinated divalent azobenzene moiety and schematic representation of their visible light triggered self-assembly.

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P56 – Manipulation of magnetic properties by supramolecular self-assembly

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Spin crossover (SCO) occurs in systems with a partial bistability between high-spin and low-spin configuration of d^4 to d^7 configured metals. External perturbations such as irradiation with light, pressure, or temperature can cause a transition between the different spin states. Recent research has focused on either inorganic clusters or polymeric materials to alter the magnetic properties.[1] We again employed the subcomponent self-assembly approach to form discrete oligonuclear complexes with readily available materials.[2] In contrast to their mononuclear counterparts oligonuclear complexes not only allow tuning of SCO-properties via *intra*molecular interactions but also via *inter*molecular interactions.

Mechanically connecting two iron(II)centres within a tensed pseudo helical structure 1 results in a novel effect of stabilising the high-spin configuration at the metal centres. Imidazole containing systems are quite ubiquitous in spin-crossover materials, combining appropriate bite angles and electronic properties to stabilise both low- and high-spin configuration. In contrast to this our complexes features nearly ideal Curie paramagnetism. Hence the high-spin state is stabilised even at very low temperatures.

Expanding this approach to pyridylimines, featuring electronic properties to only stabilise the low-spin configuration, we could stabilise the high-spin configuration. This results in a beginning spin crossover around 80 °C and solvent induced spin-crossover (see Fig. 1).

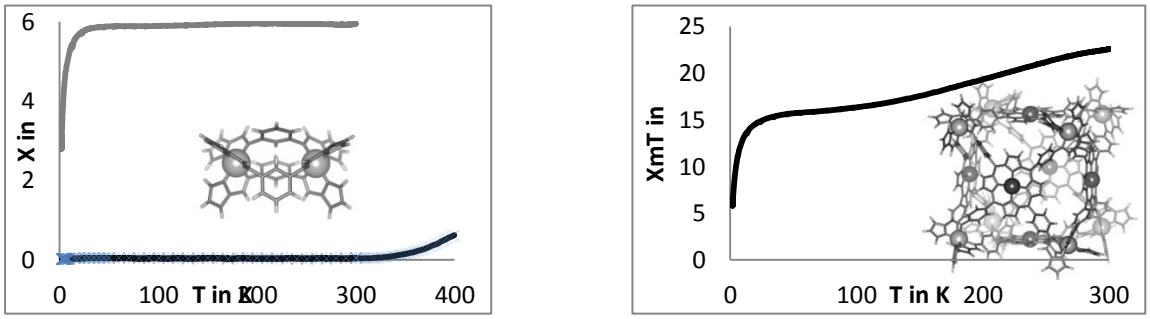

Fig. 1: Magnetic susceptibility measurements and molecular structures of 1 and its pyridylimine analogue (right) and 2 (left).

We also expanded this approach to porphyrine based tetravalent ligands to result in cube-shaped octanuclear complexes 2. While waiving the aspect of strain we nevertheless found an interesting stabilisation of high-spin configuration. Lowering the temperature from an all-high-spin-state at room temperature results in an initial broad spin crossover to a state in which three of eight metal centres are in low-spin-configuration. This state is stabilised in a range of about 60 K. Only cooling below 30 K results in a further switching to low-spin configuration at the remaining metal centres.

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P57 – On the way to patterned surfaces: deposition of dissymmetric molecules and metallosupramolecular complexes on HOPG

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One major issue of our group's research program is the investigation of diastereoselective self-assembly processes of metallosupramolecular complexes. The comparison of racemic and enantiomerically pure dissymmetrical ligands based on, e.g. the *Tröger's* base, the BINOL, or the 9,9'-spirobifluorene scaffold, reveals interesting self-sorting processes of the racemic compounds.[1]

Having learnt much about the self-assembly process we are now working on the decoration of solid surfaces like HOPG with these diastereomerically pure metallosupramolecular aggregates in order to achieve highly ordered surface patterns. Therefore, we have to modify the ligands backbone with long alkyl chains to optimize the interaction between the complexes and the surface (figure 1).

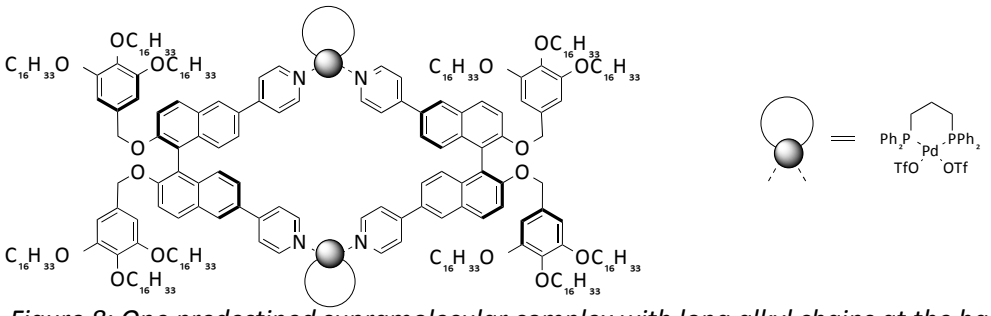

Figure 8: One predestined supramolecular complex with long alkyl chains at the backbone.

Besides, we are also interested in depositing dissymmetric molecules based on the *Tröger's* base on surfaces. Here we aim at diastereoselective self-assembly processes of the racemic compound that might also be used for further functionalization of the surface by modifying the N-N-acetal bridge with linker units that point out into the third dimension away from the surface (figure 2).[2]

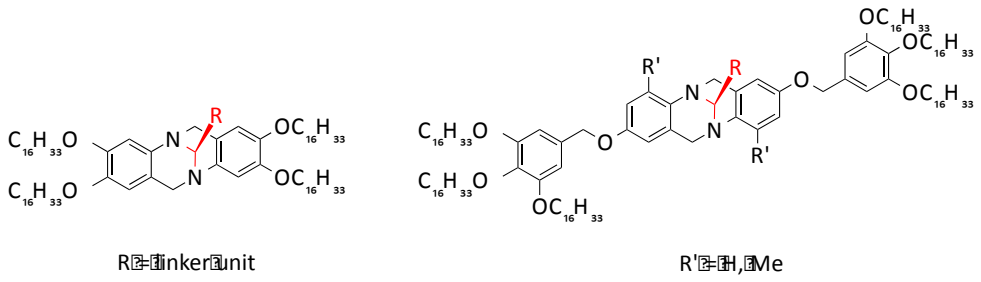

Figure 9: Two possible Tröger's base scaffolds, both with long alkyl chains and spacer units at N-N-acetal bridges (shown in red).

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P58 – Multivalent Pseudorotaxanes and Rotaxanes: Evaluation of multivalency as an organization principle

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Synthetic supramolecular complexes have the great potential to put those concepts to the test that govern much of the noncovalent chemistry in nature.[1] Supramolecular chemistry provides the possibility to design and to modify the used synthetic structures purposely. The number of binding sites as well as the spacer properties can be adjusted and varied systematically. This promises the potential to analyze multivalent interactions in detail.

For the investigation of quantitative thermodynamic data of supramolecular complexes, we turned our attention to isothermal titration calorimetry (ITC). This technique is non-destructive, noninvasive and highly accurate and therefore mainly applied to analyze molecular interactions in solution.[2,3] For this reason it is well-suited for the analysis of the presented multivalent pseudorotaxanes. The use of double mutant cycles helps to quantify the chelate cooperativity and the effective molarity of multivalent supramolecular systems.

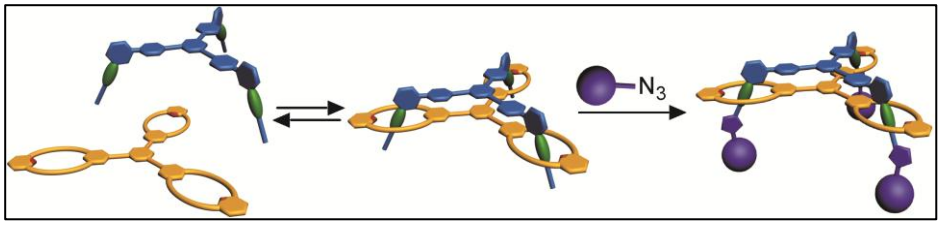

Figure 1. Formation of a trivalent pseudorotaxane und the corresponding mechanically interlocked rotaxane.

The detected enhanced binding affinities of the examined pseudorotaxanes resulting from the multivalent interaction are the basis for a highly efficient synthesis of di- and trivalent rotaxanes through stoppering the axle termini by “click” chemistry. Furthermore, the trivalent rotaxane acts as a “molecular elevator” that can be controlled by external stimuli (chloride addition and removal) which lead to a movement of the wheel along the axle.[4]

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P59 – Metallosupramolecular aggregates from *cis*-protected Pd(II) and Zn(II) ions and chiral bidentate ligands

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Self-sorting of chiral molecules is a true challenge in supramolecular chemistry due to the fact that factors like geometrical complementary of size and shape that are usually employed to achieve high-fidelity self-sorting do not really vary but only the relative spatial orientation of the components differs. If there is any self-sorting at all, one can distinguish between narcissistic self-recognition leading to homochiral assemblies or self-discrimination also called social self-sorting giving rise to heterochiral assemblies.[1] As part of our ongoing program to elucidate general rules for the diastereoselective self-assembly of metallosupramolecular aggregates we have recently tested [2.2]paracyclophane-bis(isonitril) ligands designed to coordinate to either divalent *cis*-protected [(dppp)-Pd(OTf)$_2$] ions or tetravalent palladium(II) ions. Due to its angle of 120°, 3:3 complexes with both enantiomeric and racemic ligands are formed upon coordination to *cis*-protected Pd(II) ions. Concerning the racemic ligands, self-recognition was found to be favored but not exclusive.

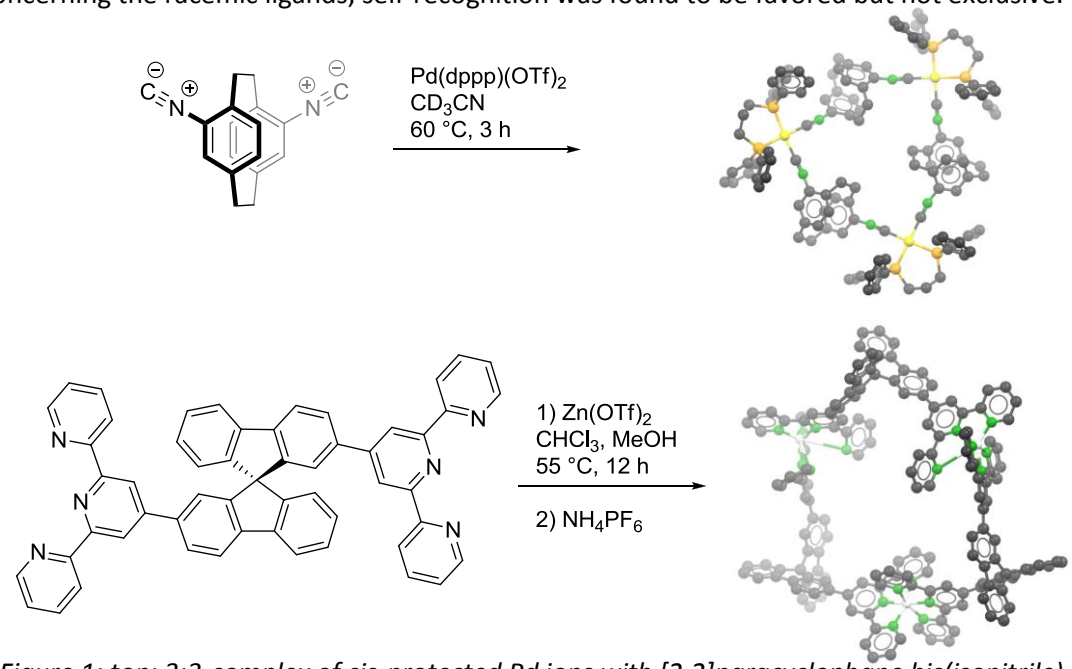

Figure 1: top: 3:3-complex of cis-protected Pd ions with [2.2]paracyclophane bis(isonitrile) ligands. bottom: 3:3-complex of 2,2'-bis(terpyidine)-9,9'-spirobifluorene ligands with Zn(OTf)$_2$.

In case of a bis(terpyridine) ligand based on a spirobifluorene scaffold we tested its coordination towards zinc(II) and Iron(II) ions. Interestingly, zinc ions seem to favor the formation of 3:3-aggregates instead of the initially expected 4:4 complex despite the fact that the spirobifluorene scaffold contains an angle of 90°. The 3:3-aggregate was analyzed by ESI mass spectroscopy and NMR-experiments including DOSY- and ^{1}H-NMR.

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P60 – Development of a new homogenous Zr-catalyst for the self-condensation of acetone

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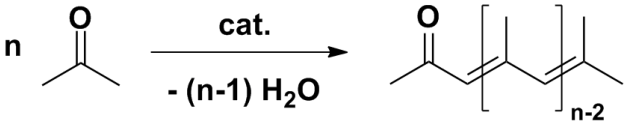
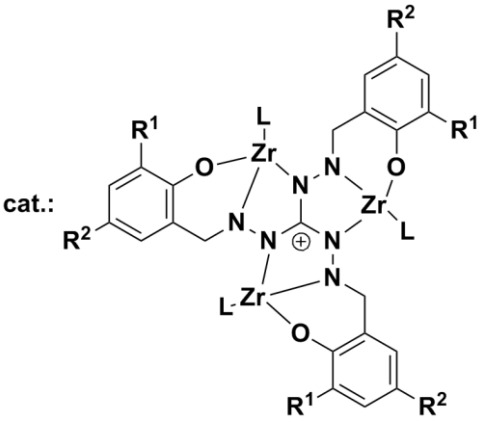
C_3-symmetric ligands based on triaminoguanidinium salts are able to coordinate three metal ions in their tris-chelating coordination pockets. They are known to form discrete coordination cages, for instance tetrahedra[1,2], an octahedron[3], or a trigonal bipyramid[4], using different metal ions such as Pd^{2+}, Zn^{2+} or Cd^{2+}. Via reduction of the imine, the flexibility and the charge per binding pocket are enhanced. Consequently, very hard metal ions like Ti^{4+} or Zr^{4+} can be coordinated. Model compounds show that the ligand coordinates three titanium ions and forms a double-decker-like structure by building oxo-bridges between two titanium atoms. Using these compounds, we could observe that the systems are active in the aldol condensation of acetone and they promise to be a suitable system for polymerization. Despite acetone is a low cost and largely available raw material, its homopolymerization is not industrially applied due to the harsh reaction conditions. Appropriate homogenous catalysts for the self-condensation of acetone are nearly unexplored.

Herein we report the development of a new homogenous Zr-catalyst which is active in the aldol condensation of Acetone.





R^1	R^2	activity
H	H	No
OH	H	No
OMe	H	Yes
H	*t*Bu	Yes
H	Br	Slightly
OMe	Br	Yes

References:

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P61 – Cooperativity effects in multivalent systems − A case study

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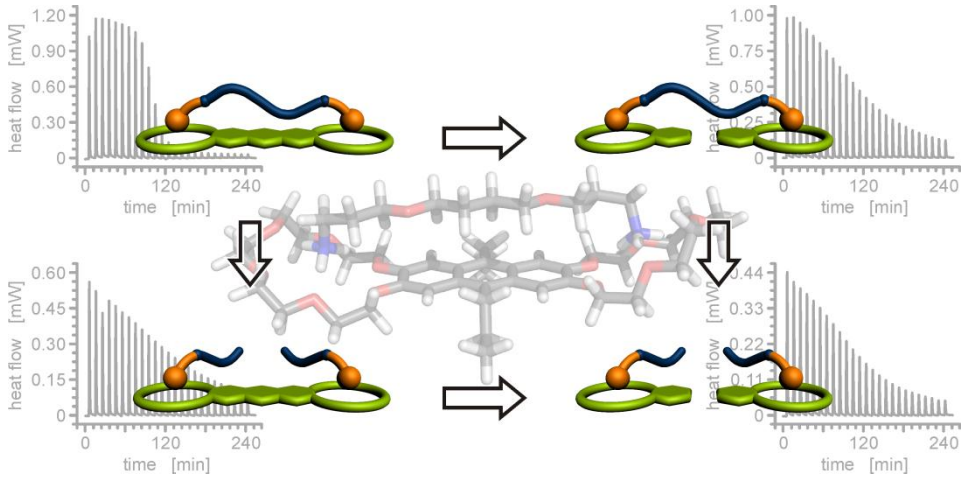
The particularly strong as well as reversible interaction in multivalent systems arises increasing interest, especially as it is progressively used in the fields of supramolecular and medicinal chemistry. To understand and quantify the unique enhancement of the binding constant *K* in multivalent systems, different cooperativity effects have to be considered individually. Besides, various possible unbound, bound and partly bound states occur during the association process of a multivalent guest to a multivalent host. The number of these states influences the value of the over-all binding constant *K* of the multivalent system by statistical factors. Hence, these statistical factors have to be quantified prior to any experimental analysis of the association process. Subsequently, a *double mutant cycle* analysis[1] may be used to quantify all cooperativity effects in the multivalent system.



We use this approach to study the cooperativity effects of divalent crown-ammonium-complexes in different solvent mixtures. Isothermal titration calorimetry is the only tool to directly and simultaneously determine the binding constant *K* as well as the binding enthalpy Δ*H* and thus derive the Gibbs energy Δ*G* and the entropy Δ*S*. Furthermore, we compare our experimental data with DFT[2] and molecular-dynamics calculations which give further insight into the processes occurring upon multivalent binding in solution.

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P62 – Novel C_2-symmetric bipyridine based ligands as building blocks for heterometallic supramolecular cages

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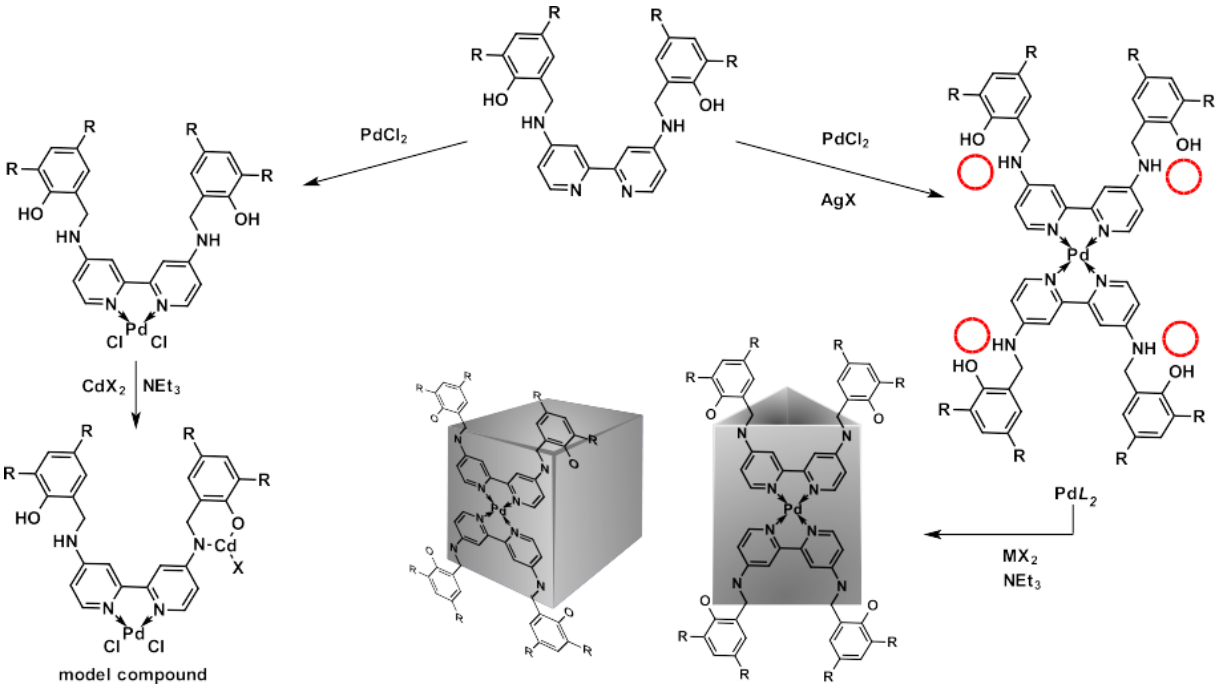
Pyridine and bipyridine ligands are widely exploited in supramolecular chemistry as ligands for the construction of networks and cages.[1,2] Herein we describe the synthesis and first applications of novel C_2-symmetric bipyridine based ligands. The conversion of 4,4'-diamino-2,2'-bipyridine and 3,5-substituted salicylaldehydes is followed by the subsequent reduction of the imine bonds. The resulting ligand is stable against moisture and consists of a flexible coordination behavior.



These C_2-symmetric ligands could be linked by Pd(II)-ions. Those PdL_2 building blocks could be connected via the N-O coordination pockets to form polyhedra with a almost closed shell, similar to those of Fujita et al, Mukherjee et al. and Smulders et al.[2-4]

To get a deeper insight into the coordination behavior and the reactivity, the synthesis of heterometallic coordination compounds on the basis of one or two of these ligands as model compounds is an important step.

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P63 – Studies on pH-Sensitive Multifunctional Supramolecular Amphiphiles

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We recently found that amphiphiles consisting of a guanidiniocarbonyl pyrrole carboxylate zwitterion carrying an alkyl or aromatic substituent at the 4-position of the pyrrole (e.g. 1) hierarchically form supra-molecular structures in a pH dependent manner in aqueous solution. The zwitterionic head forms specific, discoid dimers ($K \approx 10^{12}\ M^{-1}$ in DMSO)[1] at neutral pH. Upon addition of acid (pH < 5) or base (pH > 8) the discs disassociate due to protonation or deprotonation of the zwitterion. To obtain information of those aggregates and their inner structure we use different methods for measuring in solution (DLS, SLS, SANS, DFM) and after deposition on surfaces (AFM, TEM). The special feature of these molecules is that they can exist in three different ampiphilic forms, a cationic, an anionic and a zwitterionic one, which can be transformed into each other by external stimuli. This allows us to take a closer look at the interactions between those kinds of structures and with the solvent.

Molecules 1, 2 and 3 form colloids in neutral aqueous solution, which are stable for many days. While the neutral and basic solutions are both stable, the acidic ones start to precipitate. First results for neutral as well as for basic conditions show cylindrical structures of different sizes depending on pH range and tail group. We have indications that the formed aggregates are built out of smaller sized structures of equal shape. This results in a more complex aggregation behavior, which has to be investigated further.

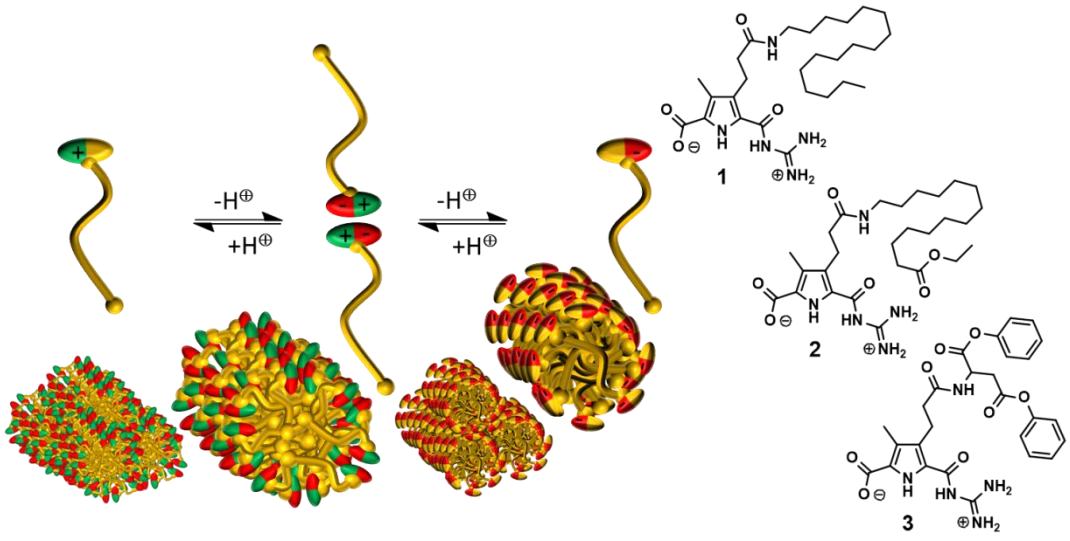

Figure 1. pH-switchable supra-structures.

References:

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P64 – Self-sorting of crown ether/secondary ammonium ion hetero-[*c*2]daisy chain pseudorotaxanes[1]

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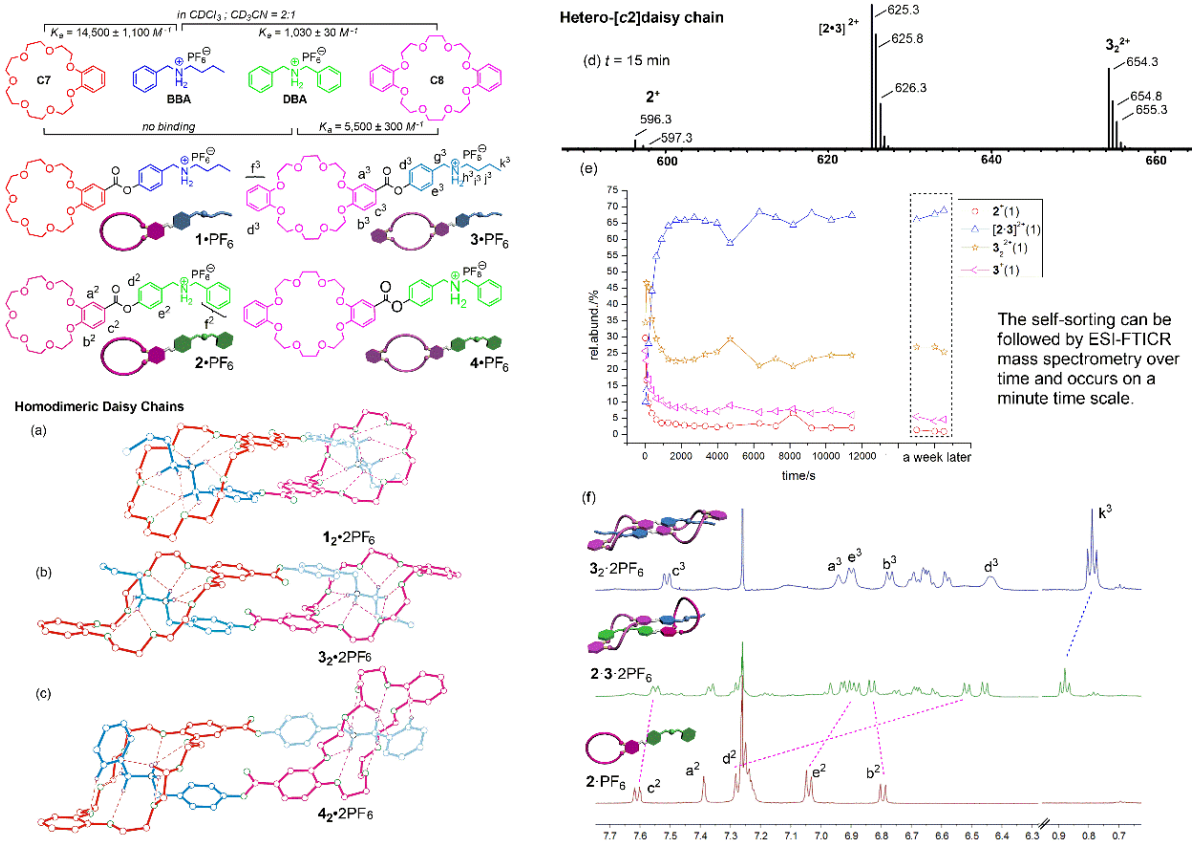
Nature efficiently and successfully assembles intricate and highly complex architectures, in which high-fidelity self-sorting is ubiquitous as the basis of the building blocks' cooperative functional interplay. Recently, we have applied the concepts of social self-sorting to pseudorotaxane assemblies based on the crown ether/secondary ammonium ion binding motifs. Four monomeric building blocks equipped with one crown ether and one secondary ammonium ion are synthesized and studied with respect to their ability to form daisy chain dimers. Two crown ethers with different cavity sizes – i.e. [21]crown-7 and [24]crown-8 – and two ammonium ions substituted with either a thin alkyl group or a more bulky benzyl group are used as the binding motifs. Self-sorting behaviour can be expected as the [21]crown-7/alkyl ammonium and [24]crown-8/benzyl ammonium binding motifs are orthogonal. Three homodimers are characterized by NMR, X-ray crystallography and ESI mass spectrometry. They are recognizable by the presence of signals for diastereotopic protons in the ^{1}H NMR spectra. The formation of hetero-[*c2*]daisy chain dimers can be monitored by NMR spectroscopy and ESI mass spectrometry and show the expected self-sorting behaviour.



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