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SwissSnowSymposium 2017

for young Chemists

Book of Abstracts

January 27–29, 2017

Hotel Alphubel
Saas-Fee, VS

Welcome to the SwissSnowSymposium 2017

Dear participants,

On behalf of the organizing committee, it is my pleasure to welcome you to the 15th SwissSnowSymposium in Saas-Fee.

We are delighted to announce that the 15th edition has exhibited a high participation rate, derived from the success of previous editions, with more than thirty contributions divided in talks and poster sessions.

This 3-day symposium will provide a high-level exchange platform to encourage integrated innovation and technology transfer within the Swiss young chemists' community, promoting the development of the Chemistry community as a whole. We will have the opportunity to share our ideas and scientific results whilst expanding our professional network in the cozy atmosphere of Hotel Alphubel. The Symposium will feature an extensive program this year covering recent advances in almost all the major fields in Chemistry.

Moreover, this event will offer the great opportunity of mixing science and research with snow and winter sports in the charming location of Saas-Fee within the Swiss Alps (Kanton Wallis). We are also convinced that the SnowSymposium is a unique combination of Snow&Science&Fun. Therefore networking and

Along with the other members of the SYCA, I would like to extend a very warm welcome to the five invited speakers: Dr. Amandine Kolleth, Dr. Magnus T. Johnson, Dr. Sebastian Wendeborn, Dr. Cheng Yi Chen, Dr. Alec Birkbeck, as well as to our generous sponsors whose kind contributions enable this event to take place.

We hope you enjoy the SwissSnowSymposium and enjoy the unique combination of Snow&Science&Fun!

Best wishes,

Cornel Fink
President, SYCA

We gratefully thank our sponsors

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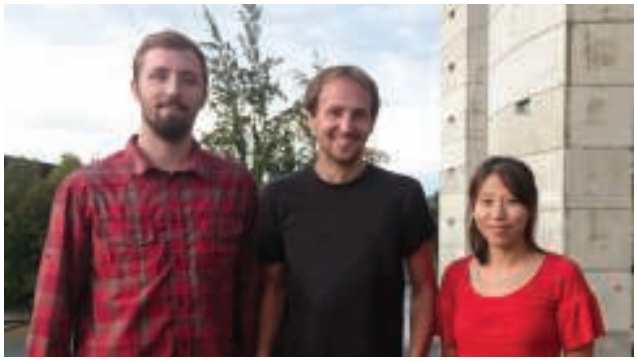

Venue Address

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House Rules

1. **Please respect the other guests, especially during the night from 23:00 until 07:00.**
2. Smoking is not allowed inside the facilities.
3. Please do not keep your wet clothes in the room, but use the drying and/or ski room.
4. Store your sports equipment in the ski room.
5. **Latest checkout is at 10:00.**
   Please ensure you have cleaned and vacated your room by that time.

Detailed Program, Snow Symposium 2017

Friday, January 27, 2017

from 17:00	**Registration, Apéro**
18:30 - 20:00	**Dinner**
20:00 - 20:10	**Break**
20:10 - 20:15	**Words of Welcome**
20:15 - 21:05	**Invited Lecture: Dr. Sebastian Wendeborn (R&D, Syngenta Crop Protection AG)** *«Sterol C(14) demethylase inhibitors as fungicides for use in crop protection»*
21:05 - 21:10	**Break**
21:10 - 22:00	**Invited Lecture: Dr. Cheng Yi Chen (R&D, Janssen)** *«Practical Organic Chemistry in Pharmaceutical Industry»*
22:00 - 22:10	**Break**
22:10 - 23:00	**Invited Lecture: Dr. Amandine Kolleth (PostDoc, Syngenta Crop Protection AG)** *«Keteniminium chemistry: a useful tool for the synthesis of small rings and aromatic derivatives»*
23:00 - 23:10	**Break**
23:10 - 00:10	**Session 1 (Chair: Cornel Fink)**
23:10 - 23:30	Ms. Florella Lucarini
23:30 - 23:50	Ms. Gurdal Yeliz
23:50 - 00:10	Dr. Almudena Gallego

Saturday, January 28, 2017

17:15 - 18:05	**Invited Lecture: Dr. Alec Birkbeck (R&D, Firmenich)** *«An interactive olfactive journey visiting some of the world's most trend setting perfumes through the eyes of the odorant molecules that made them different...»*
18:05 - 18:25	**Session 2 (Chair: Dmitry Vasilyev and Tiu Elisha Gabrielle)**
18:05 - 18:25	Dr. Jens Gaitzsch
18:30 - 19:45	**Dinner**
19:45 - 20:15	**Poster session**
20:15 - 20:20	**Photo Session**
20:20 - 21:10	**Invited Lecture: Dr. Magnus T. Johnson (Group leader, Lund University)** *«Metal-ligand cooperativity in homogeneous catalysis»*
21:10 - 21:20	**Break**
21:20 - 00:00	**Session 3 (Chair: Dmitry Vasilyev and Tiu Elisha Gabrielle)**
21:20 - 21:40	Mr. Sascha Keller
21:40 - 22:00	Ms. Bernadetta Gajewska

Detailed Program, Snow Symposium 2017

22:00 - 22:20	Mr. Samuel Lörcher
22:20 - 22:30	**Break**
22:30 - 22:50	Ms. Samantha Doninelli
22:50 - 23:10	Ms. Kristina Goncharenko
23:10 - 23:30	Mr. Felix Bobbink
23:30 - 23:40	**Break**
23:40 - 00:00	Mr. Giacomo Cecot
00:10	**Awards**

Sunday, January 29, 2017

07:30-09:00	**Breakfast**
09:00-10:00	**Checkout**
from 10:00	**Departure**

Swiss Snow Symposium 2017 - 26.-29.01.2017

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An interactive olfactive journey visiting some of the world's most trend setting perfumes through the eyes of the odorant molecules that made them different…

Dr. Alec Birkbeck

R&D, Firmenich
Alec.BIRKBECK@firmenich.com

The volatile molecules that make up the head, heart and base notes of a typical perfume are very varied in structure and volatility. Many trend setting perfumes have been created around a completely novel captive molecule or the intentional overdose of known perfumery molecules. This interactive talk will present an olfactive journey from the molecules that made Chanel No5 different in 1921 through to modern day trend setting molecules. The industrial approaches to the large scale manufacture of these key molecules will also be described.

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Sterol C(14)-demethylase inhibitors as fungicides for use in crop protection

Dr. Cheng Yi Chen

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Practical organic chemistry plays a crucial role in the contemporary drug discovery and development. Since many drugs are launched as chiral molecules, one of the key challenges for the asymmetric synthesis of drug substances is the efficient stereocontrol for the establishment of the desired chiral centers. The catalytic asymmetric reactions are highly desirable for these asymmetric syntheses since only a catalytic amount of expensive reagents/catalysts needs to be employed. In this presentation, a few novel catalytic asymmetric transformations will be illustrated for the synthesis of several structurally complex drug targets. Furthermore, a few interesting examples of heterocycle synthesis will be described.

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Keteniminium chemistry: a useful tool for the synthesis of small rings and aromatic derivatives

Amandine Kolleth[1], Alexandre Lumbroso[1], Mathilde Lachia, Gamze Tanriver[2], Saron Catak[2], Sarah Sulzer-Mossé[1], Alain De Mesmaeker[1]*

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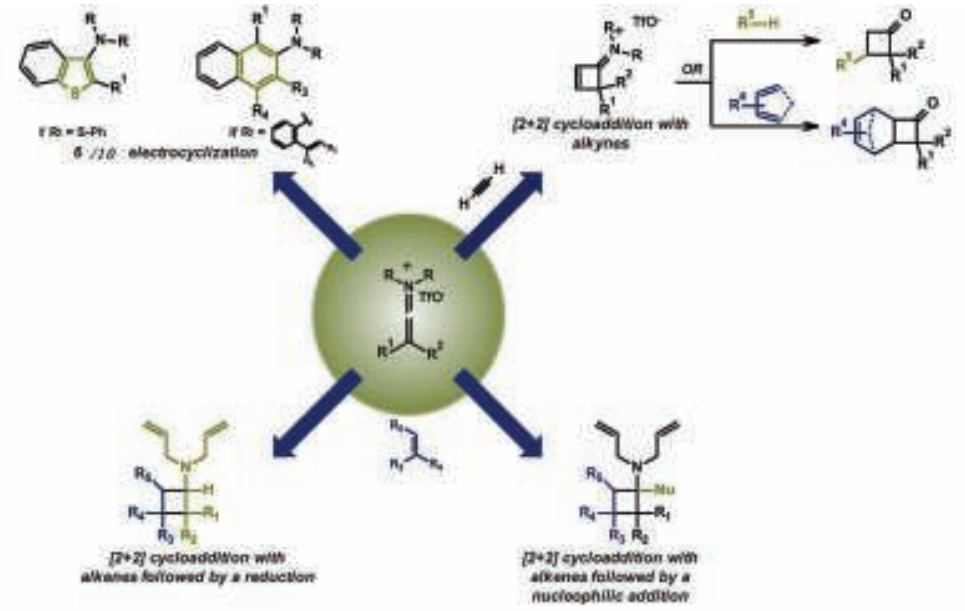
Keteniminium salts possess different types of reactivities enabling the formation of versatile valuable skeletons. Highly substituted naphthylamines as well as 3-amino-benzothiophenes are indeed easily accessible and involve keteniminium salt intermediates reacting *via* a 6π-/10π or a 6π-electrocyclization respectively. But among all the reactions involving keteniminium salts, [2+2] cycloadditions have been by far the most studied; we recently developed a [2+2] cycloaddition with alkynes affording cyclobuteniminium salt adducts which were further elaborated by [4+2] cycloaddition or Michael addition reactions using various dienes or nucleophiles. Furthermore, we also reported a one-pot sequence to obtain aminocyclobutanes, relying on [2+2] cycloadditions with alkenes followed either by stereoselective reduction or nucleophilic addition. The use of easily removable *N*-allyl protecting groups increases the potential of this method to access, in a few steps, highly functionalized cyclobutaneaminescontaining building blocks.



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Sterol C(14)-demethylase inhibitors as fungicides for use in crop protection

Sebastian Wendeborn

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π-fungicides play an important role in controlling diseases in crops. A particular important class of fungicides are the sterol C(14) demethylase inhibitors, which inhibit the oxidative demethylation of C(14) during the fungal biosynthesis of ergosterol. This talk will discuss design and synthesis of molecules acting as inhibitors of the involved cytochrome P450, 'CYP51'. In the first part of the talk, the synthetic access to pyridyl-isoxazole derivatives will be presented, with a focus on the efficient synthesis of the isoxazole ring. In the second part of the talk CH-pi interactions between C(14) demethylase inhibitors and the enzyme will be discussed and inhibitors which could engage in stronger CH-pi contacts and therefore more selective binding to the targeted P450 will be presented.

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Metal-ligand cooperativity in homogeneous catalysis

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Transition metals bearing cooperative ligands have been shown to vastly increase the scope and selectivity towards the activation of small molecules, in different fashions to traditional transition metal systems and leading to the development of new catalysts.[1] We have become interested in the chemistry of hydroxypyridines and their application as ligands in transition metal catalysed hydrogenation and dehydrogenation reactions. In particular we are concentrating on 2-pyridones, as when ligated their deprotonated form has been shown to cooperate with the metal centre in the cleavage of dihydrogen[2] and because the moiety is utilised by nature in the active site of iron hydrogenase.[3]

Initially our research has been concerned with understanding the activation of dihydrogen by metal complexes bearing pyridone ligands. Similarly to previous reports we have found that pyridone iridium complexes undergo traditional oxidative addition of H2, often leading to the dissociation of the pyridine moiety. We have used these results to influence the direction of our research, subsequently synthesising bidentate ligands which contain the pyridone moiety and exploring how iridium complexes of the ligands react with hydrogencontaining substrates.

We have also investigated a number of ligands containing the 2-hydroxypyridine moiety towards transition metal catalysed, acceptorless dehydrogenation and hydrogenation catalysis.

[1] J. R. Khusnutdinova, D. Milstein, *Angew. Chem. Int. Ed.* **2015**, *54*, 12236-12273.
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Towards a photo-driven artificial hydrogenase based on the biotin-streptavidin technology

S. Keller*, A. Pannwitz, O. Wenger and T. Ward

Swiss Nanoscience Institute, University of Basel

With the aim of exploiting sunlight as energy source to drive hydrogen production, we set out to engineer a catalytic dyad, relying on streptavidin as host protein (Sav) to precisely position a photosensitizer and a biotinylated reduction catalyst. In a biomimetic spirit, incorporation of the hydrogenase cofactor within a protein scaffold will allow to improve its performance by genetic means. To ensure timely electron-transfer between the photosensitizer and the catalyst, the ruthenium photosensitizer is covalently tethered to a cysteine on the Sav scaffold. We demonstrated by flash-quench spectroscopy that electron-transfer occurs from a biotinylated triarylamine, acting as an electron donor, to a suitably positioned photosensitizer.[1] Having demonstrated the feasibility of photo-driven charge separation using Sav as a protein scaffold, we synthesized a series of biotinylated hydrogen-reduction catalysts that use ascorbic acid as a sacrificial reductant and determined their propensity to produce dihydrogen upon visible illumination (Figure 1).

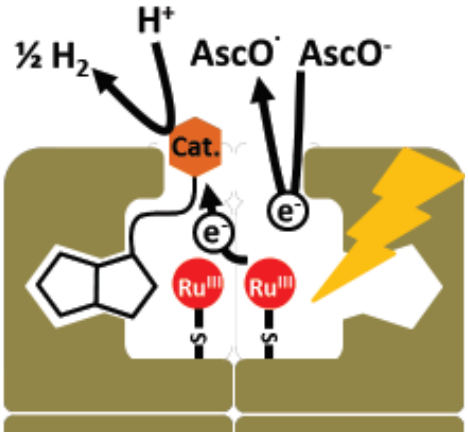

Fig 1: Schematic view of an artificial hydrogenase based on the biotin streptavidin technology. Upon light irradiation, the photosensitizer (red disk) donates an electron to the biotinylated hydrogen-reduction catalyst (orange hexagon) incorporated in streptavidin (olive). Genetic optimization allows to vary the position of both the catalyst and the photosensitizer and to provide favourable second coordination sphere interactions to favour timely electron-transfer.

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[1] S. Keller, A. Pannwitz, F. Schwizer, J. Klehr, O. S. Wenger, T. R. Ward, *Org. Biomol. Chem.*, **2016**, *14*, 7197.

*** e-mail address of presenting author** sascha.keller@unibas.ch

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Heterometallic coordination cages with unusual geometries.

Giacomo Cecot, Kay Severin.

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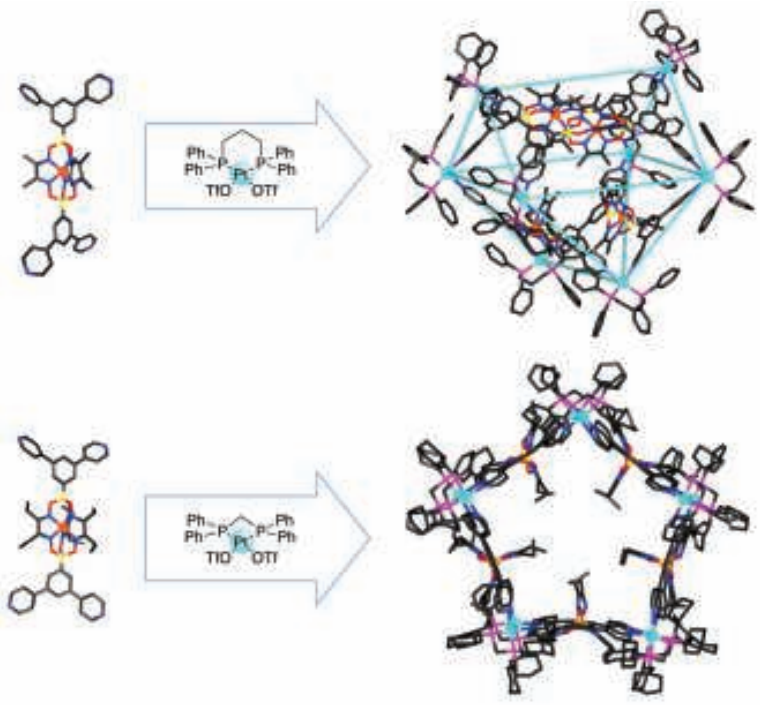
Abstract: The chemistry of coordination cages has advanced dramatically in recent years. Different synthetic approaches have been developed, allowing the efficient preparation of cages with diverse geometries and functions. Even though the rational design of coordination cages with well-defined structures has been successful in numerous cases, there is still ample room for new discoveries. We have prepared large, heterometallic coordination cages by combining clathrochelate-based metalloligands featuring terminal pyridyl groups with Pd^{II} and Pt^{II} complexes. The utilization of metalloligands instead of simple organic polypyridyl ligands resulted in the formation of uncommun structures. With 'naked' Pd^{2+} ions, we observed octahedral complexes instead of tetrahedral ones,[1] and with *cis*-blocked Pt^{II} complexes we obtained cages with unusual geometries.[2] Overall, our results provide further evidence that rather small structural modifications can have an important effect on multicomponent self-assembly reaction. The anticipation and, ultimately, the control of such effects will enable chemists to construct synthetic assemblies of unprecedented complexity and functionality.



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Design of ionic polymer catalysts for the synthesis of carbonates from CO_2 and epoxides

Felix D. Bobbink, Antoine P. Van Muyden, Paul J. Dyson

Institut des Sciences et Ingénierie Chimiques, École Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne (Switzerland).

The synthesis of cyclic carbonates from epoxides and CO_2 (CCE reaction) is an atom-efficient, scalable reaction of industrial importance. It is an important example of a catalytic reaction highlighting the utilization of CO_2 as a building block. Numerous catalysts (both metallic and metal-free)[1] have been proposed for this reaction, and in particular, ionic liquids and ionic polymers have emerged as a class of potent catalysts in this transformation. In our group, we have prepared imidazolium-based polymers (Fig. 1) incorporating functional groups that are potent catalysts for the CCE reaction.[2–4]

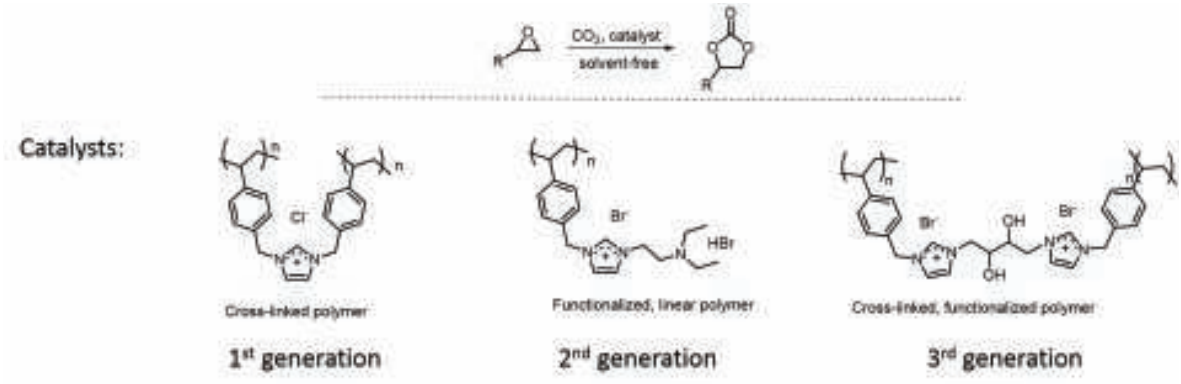

Fig. 1. Ionic polymers for the cycloaddition of CO_2 into epoxides.

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2 S. Ghazali-Esfahani, H. Song, E. Păunescu, F. D. Bobbink, H. Liu, Z. Fei, G. Laurenczy, M. Bagherzadeh, N. Yan and P. J. Dyson, *Green Chem.*, 2013, **15**, 1584.

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Hepta-coordinated Co(II) complex: a new architecture for hydrogen production

F. Lucarini, A. Ruggi

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Hydrogen is a promising potential clean source of energy which can be produced using abundant and renewable resources (e.g. water and sunlight). Water reduction catalysts are usually based on non-precious metals among which cobalt has been the most studied because of its abundance and low price. However the development of highly active and stable catalysts that can operate in purely aqueous solutions still remains a great challenge.[1]

The most active molecular cobalt catalysts reported in literature present a common architecture: a tetra- or pentapyridyl ligand inducing a distorted octahedral geometry, with the remaining coordination sites occupied by labile ligands (e.g. water).[2,3]

To further investigate the effect of coordination geometry on the catalytic activity, we designed a new ligand with six coordination sites that lead to the formation of an unusual hepta-coordinated Co(II) complex (Figure 1). Under visible light irradiation in water, this complex can efficiently catalyze the production of H_2 with a turnover number (TON) > 3000 mol H_2 (mol cat)$^{-1}$ and nearly 90% of H_2 evolved within the first hour of irradiation, i.e. a turnover frequency (TOF) > 1000 mol H_2 (mol cat)$^{-1}$ h^{-1}.

These results suggest that hepta-coordinated cobalt complexes, never used so far in the field of light-driven hydrogen evolution, represent a promising alternative platform for the development of highly active and stable photocatalysts.

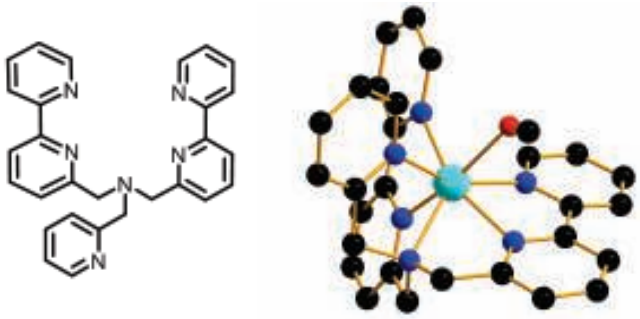

Figure 1. Ligand (left) and X-ray crystal structure of the Co(II) derivative (right).

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Synthesis of amphiphilic giant hollow helices: mimicking secondary structure formation

Samantha Doninelli, Andreas F.M. Kilbinger,

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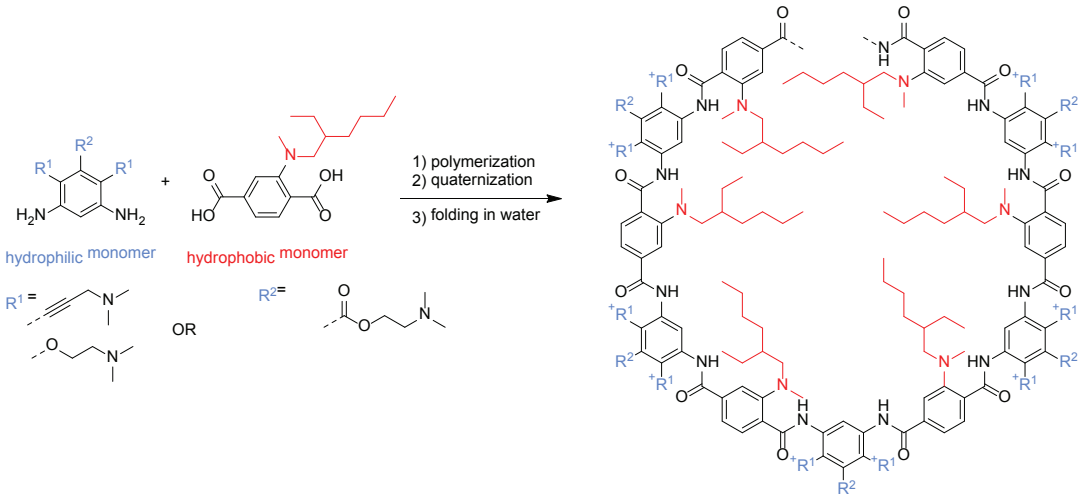
Tubes are ones of the most present structures in nature; the different size of tube determines the function of these structures. Big tubes, for example, transport blood and nanotubes are used to transport anions and cations trough the cell membrane. Over the past years many successful reports on the synthesis of tubular helices inspired by nature have been reported.
There are many different ways to synthetize a helix. Our strategy is to fold a rigid shape-persistent amphiphilic single polymeric chain. High molecular weight tube-like polymeric helices have not been reported to date. The aim of this work is to improve the hydrogen-bonded helix reported by Schulze et al.[1] via polycondensation between para-linked monomer and meta-linked monomer units. The driving force for the folding of the final structure is the side chain amphiphilicity. The polymer obtained by polycondensation of these two monomers should fold into a helical shape if exposed to water.
The aramide backbone is composed of a para-linked terephthalic acid monomer carrying a hydrophobic side chain and a meta-linked diamino monomer carrying one or two hydrophilic side chains. For this work the polymerization is based on the commercial Kevlar-synthesis (A2/B2-monomer system) because the highest molecular weights and fewest side reactions are expected for this strategy.



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Chlorophylls – a green approach to controlled radical polymerizations

Bernadetta Gajewska, Nico Bruns

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Chlorophylls are green pigments which commonly occur in nature. Despite it is 200 years since chlorophyll was discovered, it is a molecule with undiscovered properties until today. Chlorophylls are porphyrins that complex magnesium in the centre of their ring. The structure of chlorophyll is similar to heme which has been used to catalyse atom transfer radical polymerizations (ATRP).[1, 2] Shanmugam et al employed bacteriochlorophyll to initiate RAFT polymerizations induced by light.[3, 4] The catalysis of ATRP by chlorophyll has, however, not been explored. Hereby I will present the catalytic ability of chlorophylls and its derivatives in ATRP. Controlled radical polymerizations of monomers such as styrene were achieved and the reactions characterized by gel permeation chromatography and UV-vis spectroscopy.

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Make Polymer Vesicles Great Again – With the Help of Organic Chemistry

Jens Gaitzsch, Jenny Folini, Jim Anderson, Giuseppe Battaglia, Wolfgang Meier

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The chemical versatility polymers is one of the major benefits of polymersomes.[1] However, even more potential can be unlocked if polymer chemistry is combined with organic chemistry to obtain new polymers and unleash more functionalities.
Polymersomes usually have a surface without any domains, which represents a major drawback with respect to natural vesicles. We accomplished stable domains by synthesising a miktoarm star terpolymer based on dibromomaleimide (see figure part a).[2] Translated from organic chemistry it was achieved in highly selective and clean reactions. Since the polymers are now chemically linked, they cannot phase-separate, producing the stable domains on the surfaces of the vesicles.[2, 3]

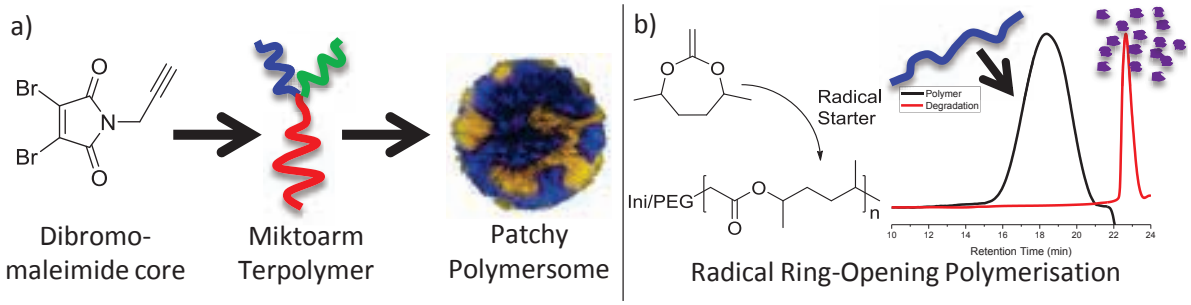

Figure 1: (a) Dibromomaleimide is the basis for a miktoarm-star terpolymer to produce polymer vesicles with stable domains. (b) Cyclic ketene acetals produce polyesters which are then degradable.

One gap in polymer science in remains in general, not only with respect to vesicles. Radical polymerisation (RP) can produce highly responsive polymers, but not biodegradable ones. The opposite is true for ring opening polymerisation (ROP). Using radical ring opening polymerisation (RROP) from cyclic ketene acetals (CKAs), degradable polymers unavailable from RP and RROP are now accessible (Figure part b). While there was only one route known to produce CKAs, we have not only improved it by introducing a new catalyst, but have also developed an entirely new synthetic pathway towards them.[4] We now synthesised and polymerised two CKAs, one responsive and one not, yielding degradable polymers inaccessible in other ways. RROP turned out to be self-controlled and thus holds a major advantage over traditional RP of (meth)acrylates. We are currently investigating block-copolymers from RROP, their self-assembly and degradation.
Both examples show how well polymer chemistry can improve if it is fruitfully combined with organic chemistry and that a new generation of polyesters is available with RROP.

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Triblock vs. Pentablock self-assembly of PMOXA(-*b*-PDMS-*b*-PMOXA)$_x$ block copolymers

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The cationic ring opening polymerisation of 2-methyl-2-oxazolines (MOXA) on bifunctional poly(dimethylsiloxane) (PDMS) macro-initiators yields amphiphilic block copolymers. Due to chain transfer reactions [1], the obtained crude block copolymer is a mixture of triblocks and pentablocks which can be separated in bulk by a new cosolvent extraction technique [2].

The pure triblock (PMOXA(-*b*-PDMS-*b*-PMOXA)$_1$) and pentablock (PMOXA(-*b*-PDMS-*b*-PMOXA)$_2$) copolymers assemble into unique but characteristic architectures. The triblock copolymers yield polymersomes, worm-like micelles or polymersomes, depending on their hydrophilic/hydrophobic weight fraction (F_{OX}, Fig. 1). Recent studies on these polymeric membranes gave detailed insight into their structure, fluidity and composition [4].

The PMOXA-*b*-PDMS-*b*-PMOXA-*b*-PDMS-*b*-PMOXA copolymers on the other hand were not reported prior to the development of the cosolvent fractionation [2] and their filmrehydration results in the formation of random polymer aggregates. Here we report the characterization and assembly of thin films with ordered, nano-sized and fine grained character. Such nano-terraced film assemblies are rare in literature and represent an inviting opportunity to study the fundamental aspects of pentablock copolymer assembly.

[1] Litt, M., Levy, A., Herz, J.: *Polymerization of Cyclic Imino Ethers. X. Kinetics, Chain Transfer, and Repolymerization,* **1975,** Journal of Macromolecular Science: Part A - Chemistry 9, 703–727.
[2] Lörcher S., Meier W.: *Cosolvent fractionation of PMOXA-b-PDMS-b-PMOXA: Bulk separation of triblocks from multiblocks*, **2016**, European Polymer Journal, accepted
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[4] Itel F., Chami M., Najer A., Lörcher S., Wu D., Dinu I. A., Meier W. P.: *Molecular Organization and Dynamics in Polymersome Membranes: A Lateral Diffusion Study*, **2014**, Macromolecules, *47*, 7588-7596

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Sulfoxide synthases: steps towards elucidating the mechanism

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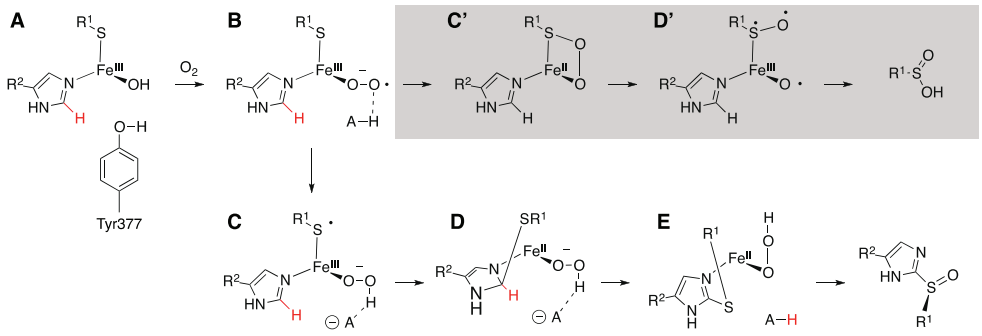
EgtB from *Mycobacterium thermoresistibile* is an unusual non-heme iron enzyme that catalyzes the formation of a sulfur-carbon bond between cysteine and N-apha-trimethylhistidine. Based on the crystal structure of this enzyme, compounded with kinetic characterization of the wild type enzyme and active site mutants we devised a model for the catalytic mechanism of this enzyme (Figure). This model predicts that the rate-limiting step includes oxidation of the substrate thiolate to a thiyl radical. To test this proposition we engineered a hydrogen bond interaction to this thiolate. This intervention does not change substrate binding but significantly reduces k_{cat}. In this presentation we discuss these observations in view of our general understanding of biocatalytic sulfur-carbon bond formation.



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Tailor-Made Concave Ligands for the Encapsulation and Functionalization of Nanoparticles.

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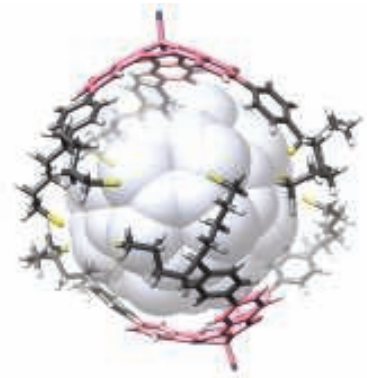
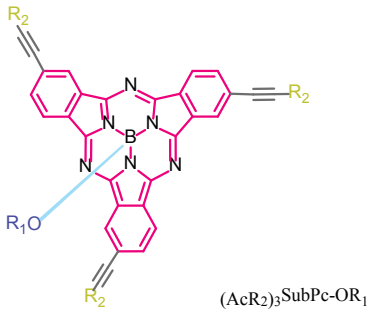
Nanoparticles are on the focus of many investigations due to its unique size-dependent electronic properties. However, the potential applications are often limited due to the challenging further manipulation. Our strategy focused on the design and synthesis of bowl-shape ligands whose complementary shape to the spherical particles would direct the stabilization of the clusters via encapsulation. The selected molecules to achieve this goal are Subthalocyanines (SubPcs). The curvature and the selective reactivity make these compounds ideal for this purpose. Modifications at the peripheral sites (-AcR_2) provide of diverse structures that would influence in the final size and stability of the NPs. Once the encapsulation process is achieved, the viable reactivity at the axial positions (-OR_1) makes possible further modifications of the bi-functionalized particles by post-synthetic methods. It would provide the tools to built-up suprastructures in a controlled way to produce 2D polymers or nanowires based on nanoparticles for technological applications.





Inspired by this vision we designed and synthesized a series of SubPcs (AcR_2)$_3$SubPc-OR_1 functionalized with different organic protected thiols in terminal positions and studied its encapsulation capabilities to form the bi-functionalized NPs.

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Adsorption of (Co)Pyrphyrins on Au(111):
The Effects of Herringbone Reconstruction and Dynamics of Metalation

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Pyrphyrin (Pyr) represents an interesting but widely unexplored molecular ligand. Instead of porphyrins which have pyrrole ring system Pyr has four pyridines as donors [1]. Metalated Pyrpyrins have recently shown promising activity for photochemical water reduction and generating alternative energy carrier H_2 in homogeneous environment. However, there are no extensive studies on their properties once deposited on metal surfaces. To fill this gap in the literature we investigate the adsorption of Pyr and the metalated one, cobalt-pyrpyhrin (CoPyr), on reconstructed Au(111) surfaces by joint computational and experimental effort. This study is motivated by the need of designing more efficient and promising water splitting devices.
We first examine the adsorption of Pyr and CoPyr molecules on reconstructed Au(111) surface using Density Functional Theory (DFT). Although, there are lots of studies related with the deposition of macrocyclic molecules on Au(111) surface, the interactions at the interface are still unclear due to the herringbone reconstruction possessed by Au surface. We find that the type of van der Waals scheme employed in DFT is important to get correct reconstruction pattern. The effects of herringbone reconstruction and adsorption registry on redistribution of the electronic states of both monomer and monolayer deposited complexes are determined. We also analyze metalation dynamics of Pyr monolayer on Au surface applying Ab-Initio Molecular Dynamics. An intermediate step during metalation is identified and determined to be a bottleneck in metalation reaction [2]. These results are in agreement with the experiments (by LEED, STM, and XPS) carried out by our collaborators [3] which will be also discussed. All the presented results suggest that CoPy can be used for hydrogen production also in the adsorbed state.

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Boronic Acids Facilitate Oxime and Hydrazone Formation, Leading to a Fluorogenic Variant

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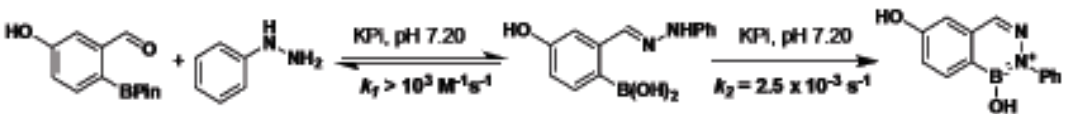
The reaction of an aldehyde with a hydroxylamine is one of the most commonly used methods for bioconjugation. Recent work by our group has shown that boronic acid groups proximal to the aldehyde greatly enhance the rate of the corresponding oxime formation. This conjugation is very stable under physiological conditions and reversibility occurs very slowly. Replacement of the hydroxylamine with a hydrazine forms the corresponding hydrazone with similar rate constants. This process is followed by an intramolecular cyclization reaction under loss of H_2O to give an aromatic, boron-substituted isoquinoline derivative. The formation of these 4,3-borazaroisoquinolines (BIQ) is much slower but irreversible. The extended aromatic system bears the opportunity to create a potential turn-on-fluorophore.



From supramolecular to covalent Polymers via disulfide crosslinking.

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Supramolecular polymers are macromolecules obtained by the self-assembly and self-organization of repeating, non-covalently linked units.[1] The structural and functional properties of supramolecular polymers largely depend on the nature of the noncovalent interactions between the individual units. Therefore, the macroscopic properties of the system are strongly dependent on the supramolecular organization and not solely defined by the properties of the molecular components.[2] Herein, we are describing a pyrene-derived trimer (**FIGURE 1**) for the preparation of covalent polymers from supramolecular scaffolds via S-S bond formation to evaluate the supramolecular structure. Pyrene molecules are connected each other by a phosphate group and the structure ends with a thiol group at the two extremities.

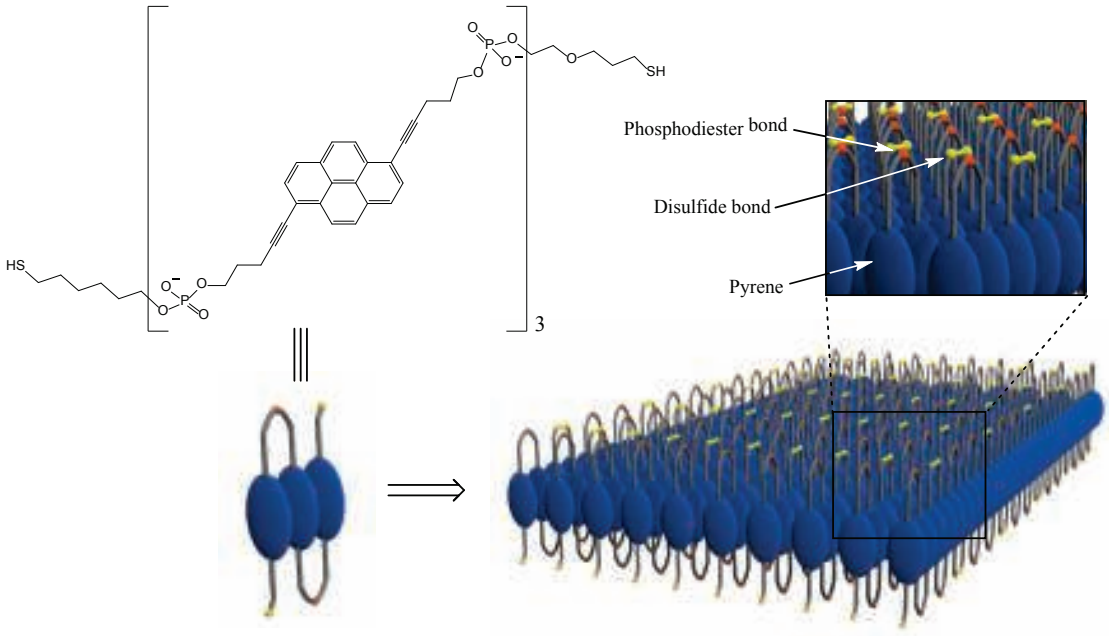

FIGURE 1: Pyrene trimer self-assembly

The aim of this project is to follow the self-assembly process in the presence of alkylthiol chains and additional phosphates, in particular if supramolecular polymers can be linked to covalent 2D polymers via disulfide formation. Spectroscopic measurements and crosslinking results will be shown.

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In vivo Assay for Artificial Metalloenzyme Evolution

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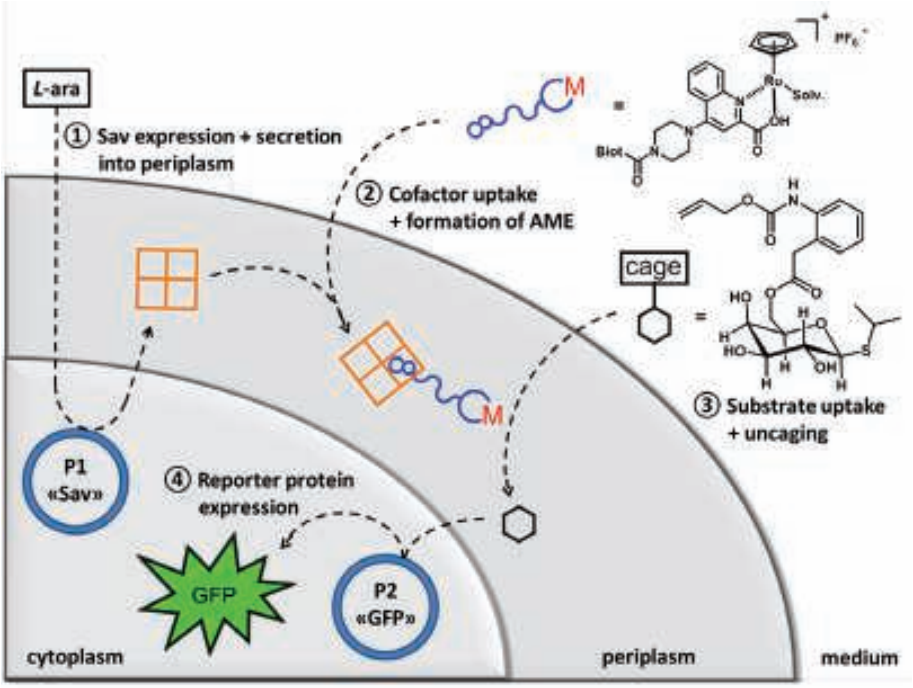
§joint project

Artificial metalloenzymes (AME)[1] allow to extend the reaction scope of natural enzymes, enabling unprecedented chemical transformations in biological systems. The performance and substrate scope of such AME can be tuned by chemical optimization of the metal cofactor or by genetic engineering of the host protein.[2] Incorporation of these AME in cellular environments bears the potential to construct powerful catalytic cascades and the development of high-throughput assays for AME evolution.

Herein, we present a two-protein *in vivo* assay consisting of an artificial allylic alkylase based on the biotin streptavidin technology and a natural reporter protein. Streptavidin (Sav) is expressed and secreted into the periplasm of *E.coli*. By incorporation of the biotinylated ruthenium cofactor [CpRu(Biot-Quinoline)][3] the AME is generated, which can uncage an allyl carbamate protected IPTG bearing a self-immolative linker. The resulting uncaged IPTG inducer leads to the over-expression of a fluorescent readout (GFP), thus potentially allowing high-throughput screening of AME activity by fluorescence assisted cell sorting (FACS).



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Heterometallic coordination cages with unusual geometries.

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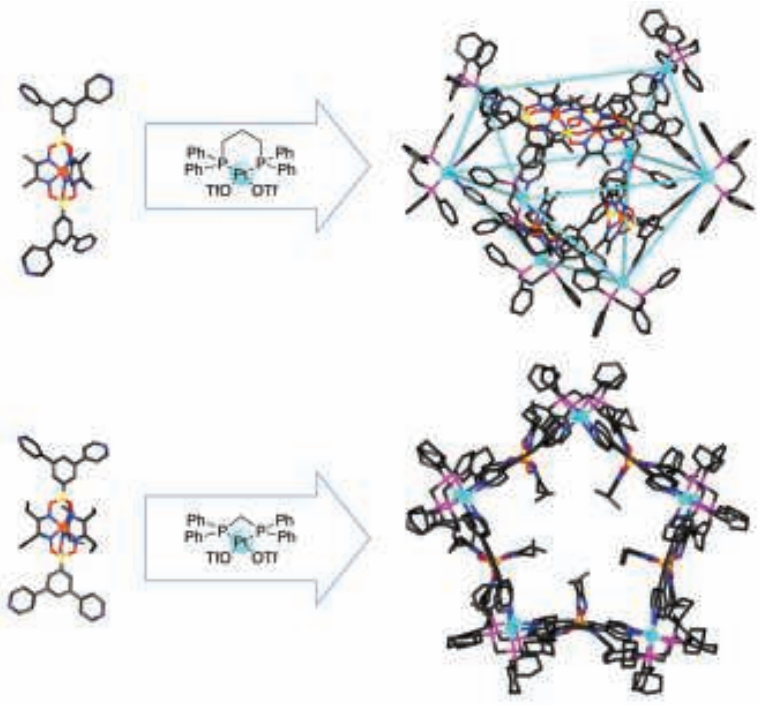
Abstract: The chemistry of coordination cages has advanced dramatically in recent years. Different synthetic approaches have been developed, allowing the efficient preparation of cages with diverse geometries and functions. Even though the rational design of coordination cages with well-defined structures has been successful in numerous cases, there is still ample room for new discoveries. We have prepared large, heterometallic coordination cages by combining clathrochelate-based metalloligands featuring terminal pyridyl groups with Pd^{II} and Pt^{II} complexes. The utilization of metalloligands instead of simple organic polypyridyl ligands resulted in the formation of uncommun structures. With 'naked' Pd^{2+} ions, we observed octahedral complexes instead of tetrahedral ones,[1] and with *cis*-blocked Pt^{II} complexes we obtained cages with unusual geometries.[2] Overall, our results provide further evidence that rather small structural modifications can have an important effect on multicomponent self-assembly reaction. The anticipation and, ultimately, the control of such effects will enable chemists to construct synthetic assemblies of unprecedented complexity and functionality.



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Fluorescent Modified Guanine Nucleotides to Probe Frameshift Mutations in DNA

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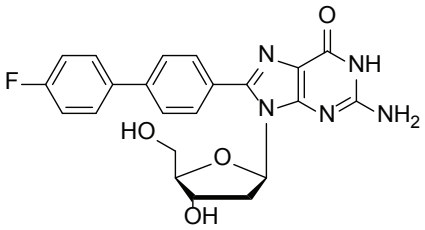
DNA frameshift mutations can form during DNA polymerase-catalyzed synthesis past chemically induced DNA damage. They may result in truncated proteins with diminished or complete loss of function. To better understand chemical aspects of how frameshift mutations arise, we synthesized a C8-biaryl modified guanine adduct and used it to model proposed steps of frameshift mutation with fluorescence spectroscopy and thermal stability analysis. Using primers with different lengths, we could show that the adduct forms a bulged out structure before a base is introduced opposite the adduct and because of the bulged out structure, translesion synthesis is stalled. The outcomes of this research include the synthesis of an environmentaly sensitive probe to detect frameshift mutations and the knowledge of how it inhibits DNA synthesis.



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ASSEMBLY OF LIGHT HARVESTING ANTENNAS THROUGH SUPRAMOLECULAR POLYMERIZATION OF AMPHIPHILIC PHENANTHRENE OLIGOMERS

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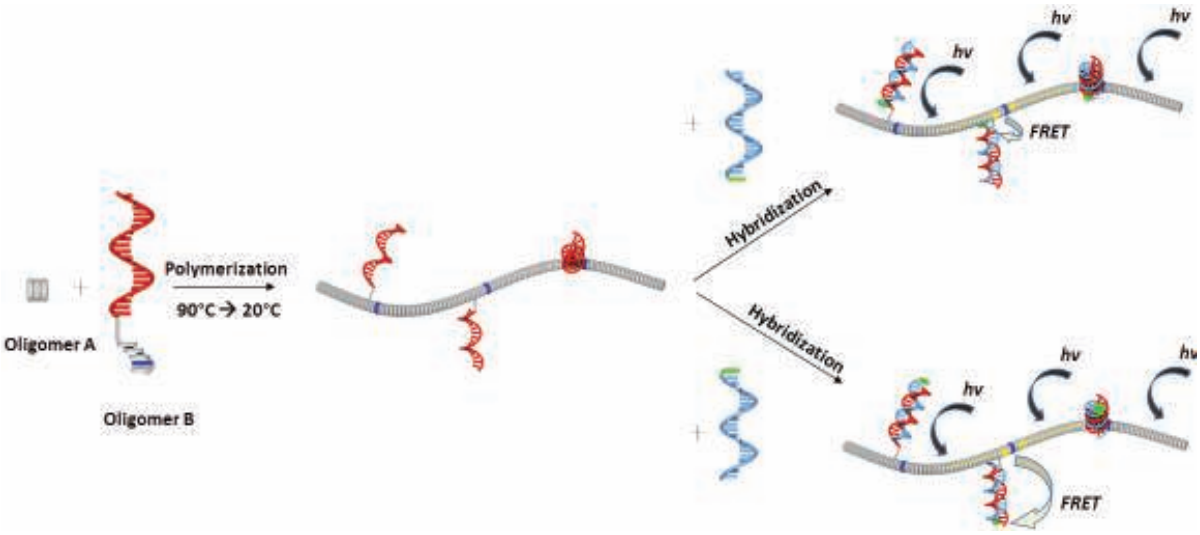
Efficient artificial light-harvesting antennas composed of multichromophoric array in a DNA scaffold are nowadays a key aspect in the supramolecular photochemistry [1]. Recently it was reported that the phenanthrene-pyrene supramolecular polymers can efficiently absorb photons which are transferred to the pyrene collection centre [2]. To expand this idea, 3,6- dialkynylphenanthrene trimer and new pyrene related oligomers were synthesized. As the DNA scaffolds are ideal platforms to organize chromophores the interesting point due to energy transfer is to introduce another acceptors in well-defined interchromophore distance from pyrene. This approach can be done by introducing complementary strand which contains appropriate chromophore in different position. Such a supramolecular complexes were investigated with different spectroscopic methods to prove efficient harvesting and transport of energy to the acceptor core through the intermediate donor-acceptor pyrene derivative.



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C-H Activation Mediated Macrocyclization: an Efficient Tool for the Synthesis of Heterocycles-Containing Macrocycles

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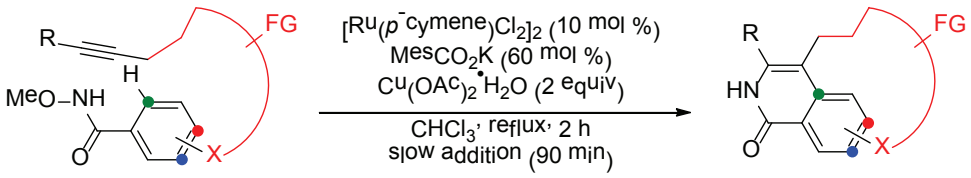
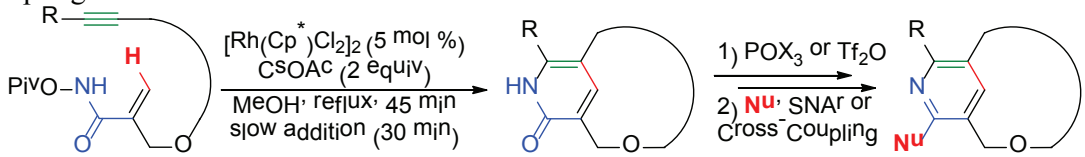
In recent years, many transformations involving C-H activation have been extensively studied.[1] However, among them, only few macrocyclization have been reported and they generally require long reaction times, high dilution conditions, high catalyst loadings and lead to poor conversions and yields. [2] As a consequence, there is a need for methods efficiently merging C-H activation and macrocyclization in order to be able to quickly access a large diversity of macrocycles with maximum efficiency.

With the goal of harnessing C-H activation reactions for the development of efficient macrocyclization processes, the Ru-catalyzed cyclization of aromatic hydroxamic acids possessing an ω-acetylenic chain was investigated. The macrocyclization features an excellent functional-group compatibility, as illustrated by the successful synthesis of a library of macrocyclic isoquinolones of different ring sizes and substitution patterns.[3]



In addition, α,β-unsaturated hydroxamic acids turned out to be easily converted to macrocyclic pyridin-2-ones in the presence of a rhodium(III) catalyst. Macrocyclic pyridones afford a convenient entry to macrocyclic pyridines after deoxyhalogenation followed by either cross-couplings or SNAr.



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Triblock vs. Pentablock self-assembly of PMOXA(-*b*-PDMS-*b*-PMOXA)$_x$ block copolymers

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Multifold-Linked Fe(II) Terpyridine Cage Complexes for Information Storage Systems

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The ongoing miniaturization of electronic devices gives rise to the field of molecular electronics where existing components like wires, switches, memory devices, etc. are mimicked by molecules. Due to several physical properties metal complexes got interesting in this field. Especially iron terpyridine complexes reached high interest for information storage systems as they possess the ability to undergo spin crossover (SCO) phenomena and they have special photo-physical properties.

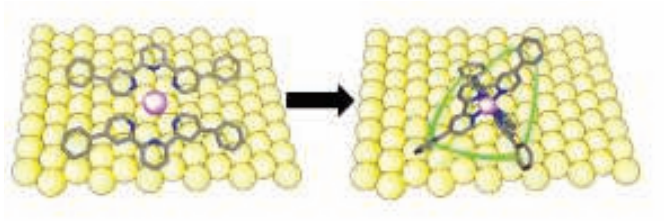

Figure 1: General concept to prevent the planar absorption on a surface.

Bis-terpyridine iron complexes tend to adsorb flat on metal surfaces. The idea of the proposed interlinked hexadentate bis-terpyridine ligand is to stabilize the corresponding complex in octahedral geometry to make it rigid enough while immobilizing on a gold (111) surface via Electron-Spray-Ionisation (ESI). Then, SCO properties are analysed using a Scanning Tunnelling Microscope and using the different colour of the different spin states of the complex.

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Screening for Potential Catalysts for Selective Formic Acid Dehydrogenation of the type [Cp*Ir(N,N)Cl]

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Catalytic carbon dioxide reduction and selective formic acid dehydrogenation are considered as potential techniques to store hydrogen in an industrial scale and by that contributing to a future hydrogen economy.[1] Many homogeneous catalysts are known to catalyze the decomposition reaction.[2, 3] A large group is based on iridium complexes with the general formula [Cp*Ir(N,N)Cl], where Cp* is cyclopentadienyl, and N are nitrogen donor ligands.[4] The nitrogen can be donated by two monodentate ligands or one bidentate chelating ligand. Especially bidentate ligands in combination with Ir-Cp* displayed excellent performance in literature, [5, 6] therefore we focused our efforts in this direction and prepared numerous compounds, exhibiting this feature. The nitrogen donor atoms comprised primary, secondary, or tertiary amines as well as nitrogen which are port of aromatic structures. Furthermore, we synthesized a series of rhodium analogues, due to their similar chemical properties to iridium and tested the compounds in the same manner. It can be stated that the activity and stability was in all cases inferior compared to the iridium complexes.

The compounds were tested primarily towards their formic acid dehydrogenation ability. Therefore, a defined amount of precatalyst was added to a medium pressure sapphire tube, mixed with water and finally the substrate, formic acid, was added to the tube, before it was sealed. The progress of the reaction was followed with two different techniques by measuring the pressure increase over time and also by NMR spectroscopy (Figure 1), taking scans in regular intervals to obtain profound kinetic information about the dehydrogenation reaction when conducting the experiment at different temperatures.

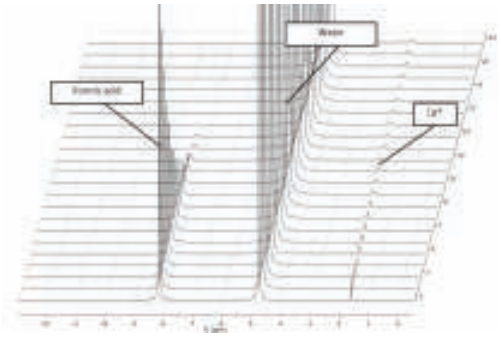

Figure 1 ^{1}H NMR (400 MHz, 10 mm) stacked spectra; 4,5 M FA in D_2O at 60°C; c(IrCp*) = ethylenediamine = 0,009 M; FA dehydrogenation is recorded as a function of time; the interval between two consecutive spectra are 450 s;

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Neutral Radicals Derived From Imidazolium Dyes

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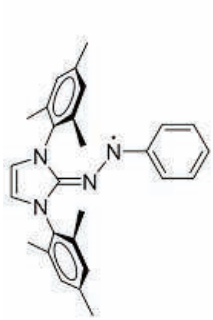
The synthesis and the characterization of a new class of aminyl radicals is reported. The neutral monoradical **1** was obtained by reduction with potassium of azoimidazolium dye featuring N-mesityl substituent at the heterocycle. Structural, spectroscopic and computational data suggest that the spin density is centered on the nitrogen atom next to the imidazolin-2-iminato group. Furthermore, we have shown that the reduction of a dimeric dye with an octamethylbiphenylene bridge between the azo groups results in the formation an open-shell diradical (**2**). Compound **2** is structurally related to compounds of the formula $[R_2N\text{-}(C_6H_2R'_2)_2\text{-}NR_2]^{2+}$, which have received considerable attention in recent years. A unique feature of **2** is the fact that it has an overall charge of zero, as opposed to +2, and strong diradical character. Both, the monoradical **1** and the diradical **2** were found to display high stability in solution as well as in solid state. The stability can be attributed to the steric shielding of the N-aryl substituents, as well as to the stabilizing effect of the imidazolin-2-iminato group. Potential applications of these new aminyl radicals (e.g. as as electrochromic dyes) are currently explored in our laboratory.



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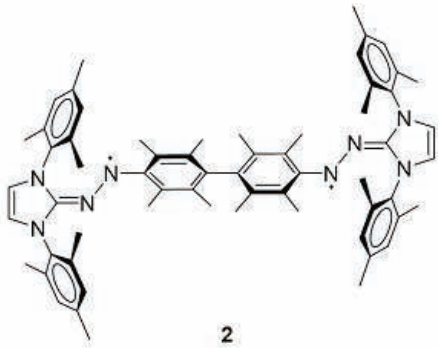

2

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