SCS
Swiss Chemical
Society

Swiss Young
Chemists' Association

13th Swiss Snow Symposium

for young Chemists

Book of Abstracts

January 23–25, 2015

Hotel Alphubel
Saas-Fee, VS

Welcome to the 13th Swiss Snow Symposium

Dear participants,

On behalf of the organizing committee, it is my pleasure to welcome you to the 13th Swiss Snow Symposium in Saas-Fee.

We are honored to announce that the 13th edition has exhibited a high participation rate, derived from the success of previous editions, with more than forty contributions divided in numerous talks and poster sessions.

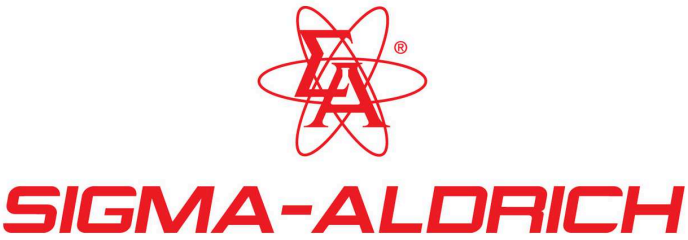
This 2-day Snow Symposium will provide a high-level exchange platform to encourage integrated innovation and technology transfer within the Swiss young chemists' community, promoting the development of the Chemistry community as a whole. We will have the opportunity to share our ideas and scientific results while expanding our professional network in the cozy atmosphere of hotel Alphubel. The Symposium will feature a formidable broad 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 (canton Wallis).

Along with the other members of the SYCA I would like to extend a very warm welcome to the four invited speakers: Prof. Sivula, Dr. De Mesmaeker, Dr. Henning, and Dr. Ruggi and to the generous sponsors that thanks to their contributions, this event can take place.

Simona Mazza
President, SYCA

We gratefully thank our sponsors



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Organizing Committee

Simona Mazza, President, SYCA
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Venue Address

Hotel Alphubel
CH-3906 Saas-Fee VS
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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.

Friday, January 23rd

From 17.00	**Registration, apéro and collecting posters**
18.45-20.15	**Dinner & Welcome Word, Simona Mazza**
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22.00-23.00	**Invited Lecture, Dr. Albert Ruggi, University of Fribourg** "Spot the Magic Dot! Quantum Dots towards therapeutics and artificial photosynthesis"
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21.30-22.30	**Invited Lecture, Dr. Jacob Jessen Henning, University of Zürich** "Synthetic Analogs of Diphosphoinositol Polyphosphates"
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23.00-23.15	Kiril Tishinov, University of Basel
23.15-23.30	Michel Rickhaus, University of Basel
23.30-23.45	Thomas Di Franco, EPF Lausanne
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Sunday, January 25th

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From 10.00	**Departure**

13th Swiss Snow Symposium

Controlling morphology and self-assembly in solution-processed semiconductor devices

Kevin Sivula
Laboratory for Molecular Engineering of Optoelectronic Nanomaterials, Institute of Chemical Sciences and Engineering, École Polytechnique Fédérale de Lausanne (EPFL), Station 6, 1015-Lausanne, Switzerland

The development of semiconducting materials that can be solution-processed into functional thin-films at low temperature, while simultaneously providing excellent device characteristics, represents a significant challenge for materials chemists and engineers. Attaining this goal will provide access to low-cost, large area and flexible displays, sensors and solar cells. In this presentation I will present the challenges to enable high performance in solution-processed semiconductors and highlight our group's approach to control morphology, self-assembly, and interfaces of different classes of solution-processable semiconductors based on their dimensionality: from 0-D oxide and sulfide nanoparticles to 1-D conjugated polymers and 2-D transition metal dicalcogenide nanosheets.

Further, I will show how our approaches allow for insight into the nature of the semiconductor band gap, light absorption, charge transfer, and carrier transport in functional thin films, and indicate routes for improvement. In addition, the application of our material systems in functional devices especially for solar energy conversion will be emphasized.

Recent Publications:

(1) Gasperini, A.; Sivula, K. Effects of Molecular Weight on Microstructure and Carrier Transport in a Semicrystalline Poly(thieno)thiophene. *Macromolecules* **2013**, *46*, 9349-9358.
(2) Sivula, K. Metal Oxide Photoelectrodes for Solar Fuel Production, Surface Traps, and Catalysis. *J. Phys. Chem. Lett.* **2013**, *4*, 1624-1633.
(3) Gasperini, A.; Bivaud, S.; Sivula, K. Controlling conjugated polymer morphology and charge carrier transport with a flexible-linker approach. *Chem. Sci.* **2014**, *5*, 4922-4927.
(4) Guijarro, N.; Prévot, M. S.; Sivula, K. Enhancing the Charge Separation in Nanocrystalline Cu_2ZnSnS_4 Photocathodes for Photoelectrochemical Application: The Role of Surface Modifications. *J. Phys. Chem. Lett.* **2014**, 3902-3908.
(5) Yu, X.; Prévot, M. S.; Sivula, K. Multiflake Thin Film Electronic Devices of Solution Processed 2D MoS_2 Enabled by Sonopolymer Assisted Exfoliation and Surface Modification. *Chem. Mater.* **2014**, *26*, 5892-5899.

13th Swiss Snow Symposium

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Spot the Magic Dot!

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Quantum Dots are semiconductor particles of nanometric size. Because of their small size, they present peculiar properties due to the quantum confinement effect: their fluorescence emission and redox properties can be tuned with size, thus enabling to obtain luminophores with tailored properties. Together with their photostability and high optical efficiency (in the presence of suitable capping units), the possibility of finely tuning optoelectronic properties during the synthesis makes them ideal candidate for many applications. In fact, Quantum Dots have been recently used for a variety of scopes: among the most intriguing applications it is possible to mention medical diagnostic (as luminescent imaging agents), realisation of optoelectronic devices and, more recently, sensitizers for solar cells.[1]

We are currently investigating the photochemical properties of systems based on Quantum Dots functionalised with transition metal complexes, which find applications for the development of phototherapeutical agents and in artificial photosynthesis.

The realisation of light-driven systems capable of releasing small bioactive molecules (like CO and NO) is a very active research field. The possibility of inducing CO and NO release upon irradiation with visible light constitute an important goal for photomedicine. The systems realised so far usually require the excitation with UV or blue light, making them unsuitable for practical applications.[2] By using Quantum Dots functionalised with Mn(I) complexes we were able to develop the first example of a system which releases CO upon photoexcitation with green light (510 nm) with a superior efficiency (200%) with respect to the pristine Mn(I) complex.

Artificial photosynthesis (i.e. the light-driven splitting of water to generate hydrogen and oxygen) is undoubtedly one of the Holy Grails of modern research.[3] In the last three years some Quantum Dots-based systems have been reported, capable of reducing protons to hydrogen in the presence of sacrificial species.[4] However, no systems are known capable of performing water oxidation (a crucial step towards water splitting). We have recently studied the electron transfer process of Quantum Dots conjugated with Ir(III) complexes, which are suitable for water oxidation.

The results obtained so far in these investigations will be presented, pointing out the challenges and the perspectives of such fascinating systems, lying between nanotechnology and coordination chemistry.

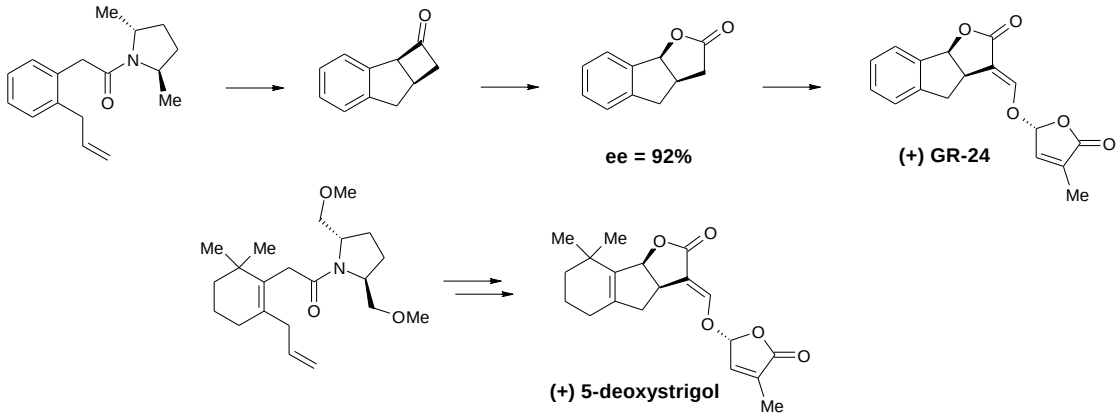
13th Swiss Snow Symposium

Strigolactones derivatives for Crop Enhancement Applications

Alain De Mesmaeker
Syngenta Crop Protection Research, Stein, Switzerland

The lecture will be devoted to our progress in the field of structural modifications of phytohormones for Crop Enhancement, in particular to the last discovered ones, namely the Strigolactones. Crop Enhancement under sub-optimal environmental conditions as cold/heat stress and drought is a very challenging area of research to secure high crop yield. Phytohormones are key players in the responses of plants to environmental changes. However, structural modifications of the natural phytohormones are needed to transform them into potential commercial compounds for abiotic stress management.

The roles of Strigolactones as key signalling molecules in plants will be briefly reviewed. A novel approach for the stereoselective synthesis of modified and natural Strigolactones using intramolecular (2+2) cycloadditions of ketenes and ketene iminiums salts to C=C double bonds will be discussed together with some data on the biological activity of novel derivatives. Additional applications of ketene iminiums salts for the synthesis of Strigolactones derivatives and for other biologically active compounds will be presented.



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A novel approach toward the synthesis of strigolactones through intramolecular (2+2) cycloaddition of ketenes and ketene-iminiums to olefins. Application to the asymetric synthesis of GR-24, M. Lachia, P. M. J. Jung, A. De Mesmaeker, Tetrahedron Lett., 53,4514, (2012)
6π/10π-electrocyclization of ketene-iminiums salts for the synthesis of substituted naphthylamines, E. Villedieu-Percheron, S. Catak, D. Zurwerra, R. Staiger, M. Lachia, A. De Mesmaeker, Tetrahedron Lett., 55, 2446, (2014)
Synthesis of strigolactones analogues by intramolecular (2+2) cycloaddition of ketene-iminium salts to olefins and their reactivity on *Orobanche cumana* seeds, M. Lachia, H. C. Wolf, A. De Mesmaeker, Bioorg. Med. Chem. Lett., 24, 2123, (2014)
Asymmetric synthesis of the four stereoisomers of 5-deoxystrigol, M. Lachia, P.Y. Dakas, A. De Mesmaeker, *Tetrahedron Lett., in press.*

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Synthetic Analogs of Diphosphoinositol Polyphosphates

Henning Jacob Jessen
University of Zürich, Department of Chemistry, 8057 Zürich, Switzerland

Diphosphoinositol Polyphosphates ($InsP_7$, $InsP_8$) are water-soluble second messengers derived from the *myo*-inositol scaffold. In contrast to inositol polyphosphates they harbor one or multiple high-energy P-anhydride bonds. Due to this special feature, they are difficult synthetic targets. Moreover, since they only occur in low concentrations in nature, their study has been significantly hampered by a lack of readily available material.

$InsP_7$ and $InsP_8$ have been shown to play roles in diverse cellular functions, such as vesicle trafficking, apoptosis, regulation of cell energy homeostasis and regulation of PH domains. Especially $InsP_7$ mediated inhibition of Akt signaling by downregulation of Akt phosphorylation has received significant attention, since IP6K1 KO mice displayed a lean phenotype on high-fat diet.
In order to study the function of $InsP_7$ and $InsP_8$ in more detail, chemical tools are in high demand. It is conceivable, that similar tools as already available for inositol polyphosphate or phosphatidyl inositol polyphosphate studies will be helpful in understanding the function of $InsP_7$ and $InsP_8$.

In this study, we will present novel chemical tools derived from our total synthesis program. These tools include photocaged $InsP_7$, permeabilized $InsP_7$ and heavy isotope labeled analogs. Initial biological evaluations will be presented in order to showcase the utility of these compounds.

Acknowledgements: This work is funded by the Swiss National Science Foundation SNF (PZ00P2_136816).

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4. H.Wang, J. R. Falck, T. M. T. Hall, S. B. Shears (2012) Nat Chem Biol 8: 111-116.
5. S. Capolicchio, D. T. Thakor, A. Linden, H. J. Jessen (2013) Angew. Chem. Int. Ed. 52: 6912-6916
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DOI: 10.1002/anie.201404398

Flow photochemistry

Andreas B. König and Christian G. Bochet

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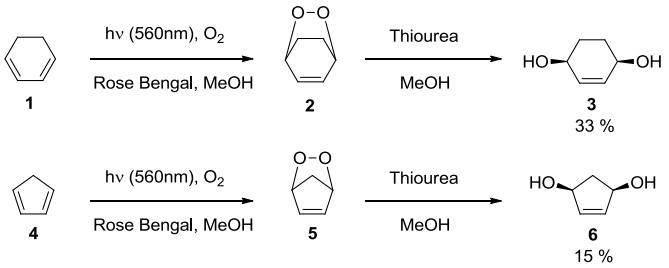
Singlet oxygen is a promising reagent in organic synthesis, since it is very reactive, readily available and inexpensive. The breakthrough started with the pioneering work of Foote and Wexler[1] that postulated $^1O_2$ as the reactive intermediate in solution by either a photochemical reaction or a chemical reaction using hypochlorite and hydrogen peroxide. These findings revealed its importance in organic chemistry as a reagent and several different reaction modes have been described. The most popular are: (a) the ene (or Schenck) reaction with alkenes to afford allylic hydroperoxides, (b) the [2+2] cycloaddition with enol ethers or enamines to form dioxetanes, and (c) the [4+2] cycloaddition with conjugated dienes or anthracenes to yield endoperoxides.

However, most industrial photochemical transformations suffer from poor economics and complex scalability. Lapkin *et al.*[2] compared the sensitized photooxygenation of α-pinene in different continuous flow reactors. In their work optimal performance was achieved with microstructured setups. Moreover, the spectral properties of the emission source as well as elevated oxygen pressure were essential to obtain high conversions.

The ultimate goal of this project is to find a method for the efficient photooxygenation in a continuous flow microreactor. Thereby, cyclohexadiene **1** and cyclopentadiene **4** were chosen as model substrates and Rose Bengal was used as a sensitizer. The mixture was irradiated under flow conditions with a LED lamp at 560 nm (Scheme 1). The formed endoperoxides **2** and **5** were then directly reduced by thiourea.



Scheme 1: Photooxygenation in a continuous flow microreactor.

We have successfully synthesized diol **3** and **6** under flow conditions in 33 % and 15 % yield, respectively. When elevated oxygen pressure was applied, only poor conversion was observed. Therefore, we tried to reduce the oxygen flow (48 µl/min) using a backpressure regulator. It became apparent that the chosen channel length of 8 cm was not appropriate. Thus a microreactor with a path length of 3 m was chosen for further experiments, and these results are under current investigations.

[1] Foote, C. S.; Wexler, S. *J. Am. Chem. Soc.* **1964**, *86*, 3879.
[2] Loponov, K. N.; Lopes, J.; Barlog, M.; Astrova, E. V.; Malkov, A. V.; Lapkin, A. A. *Org. Process Res. Dev.* asap.

Target Profiling of the Neuritogenic Natural Product, Withanolide A.

Erika A. Crane,[a] Wolfgang Heydenreuter,[b] Elma Mons,[a] Stephan A. Sieber,*[b] and Karl Gademann*[a]

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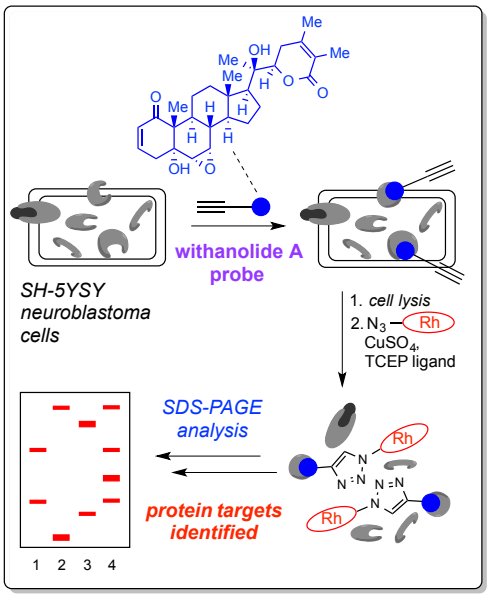
[b]Department of Chemistry, Centre for Integrated Protein Science CIPSM, Institute for Advanced Studies IAS, Technische Universität München, Lichtenbergstraße 4, 85747 Garching, Germany



Over the past century, there has been a worldwide escalation in the prevalence of neurodegenerative diseases, such as Alzheimer's, Parkinson's and Huntington's disease.[1] There are still no cures for these disorders and current therapeutics are only palliative. Emerging treatment approaches are focusing on small molecules that mimic neurotrophic properties of current polypeptidal therapeutics, as they possess inherently better pharmacological properties, mainly the ability to cross the blood-brain barrier.[2] We aim to take this further, utilizing these small molecules to probe the pathogenesis of neurodegeneration. We first isolated known neurotrophic agent, withanolide A, from the ayurvedic herb, ashwagandha root (*Withania somnifera*).[3] We then synthesized six molecular probes modified with an alkyne linker at various positions, and screened these utilizing "tag-free" activity-based protein profiling (ABPP)[4] in collaboration with the Sieber group. Initial protein target hits of interest include Transketolase, Retinal Dehydrogenase 1, Cytoskeleton-associated protein 4, and Glucocorticoid receptor. The overarching aim of this project is to utilize a multidisciplinary combination of organic synthesis and chemical biology for the advancement of neurodegenerative disease research.

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[2] Jessen, H. J.; Barbaras, D.; Hamburger, M.; Gademann, K. *Org. Lett.* **2009**, *11*, 3446. and references therein.
[3] Jain, S.; Shukla, S. D.; Sharma, K.; Bathnagar, M. *Phytother. Res.* **2001**, *15*, 544.
[4] Bottcher, T.; Sieber, S. A. *Mol. Chem. Commun*. **2012**, *3*, 408. and references therein.

Synthesis of triazenes with nitrous oxide

G. Kiefer, T. Riedel, P. J. Dyson, R. Scopelliti, and K. Severin
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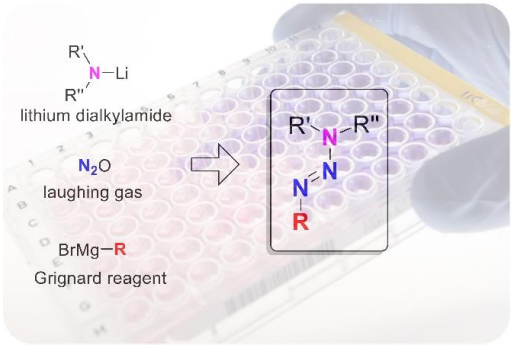
Chemical reactions with N_2O typically proceed by oxygen atom transfer and liberation of N_2. Thus, there are very few examples of reactions involving the utilization of nitrous oxide as nitrogen donor. **We invented a new method for the synthesis of triazenes using nitrous oxide as a building block.** Triazenes are valuable compounds in organic chemistry and numerous applications have been reported. Furthermore, triazenes have been investigated extensively as potential anti-tumor drugs, and the triazenes dacarbazine and temozolomide are currently used in the clinic for the treatment of various types of cancer.

Nitrous oxide mediates the coupling of lithium amides and organomagnesium compounds while serving as nitrogen donor. Despite the very inert character of nitrous oxide, the reactions can be performed in solution under mild conditions. A key advantage of the new procedure is the ability to access triazenes with alkynyl and alkenyl substituents. These compounds are difficult to prepare by conventional methods because the required starting materials are unstable. Besides representing interesting starting materials for organic synthesis, some of the new alkynyltriazenes were found to display high cytotoxicity in *in vitro* tests on ovarian and breast cancer cell lines. It is conceivable that new anti-cancer lead compounds can be found by a more thorough biological screening of these compounds.



Patent (pending): G. Kiefer, K. Severin, *Preparation and Medical Use of Triazenes*, PCT/EP2014/001773.

Publication: G. Kiefer, T. Riedel, P. J. Dyson, R. Scopelliti, K. Severin, *Ang. Chem. Int. Ed.* **2014**, 53, *early-view (online)*.

Plenary Lecture, Talk

Broadband Dye-Zeolite L Composites for Luminescent Solar Concentrators

Pengpeng CAO[1], André Devaux[1], Gion Calzaferri[2], Dominik Brühwiler[3], Peter Belser[4] *

[1]University of Fribourg, [2]University of Berne, [3]Zurich University of Applied Sciences, ZHAW, [4] Peter Belser

The concept of luminescent solar concentrators can be traced back to the 1970s and involves using inexpensive polymer-based devices to concentrate sunlight onto photovoltaic cells. However, several major challenges such as limited stability of the luminescent organic species, and high self-absorption, which kept LSCs from being widely used. The advent of advanced host-guest materials and sophisticated photon transport simulation models renewed interest in this technology. [1,2,3]

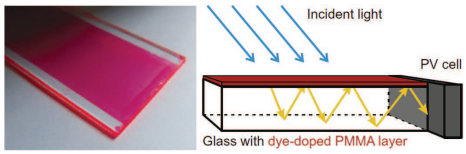


Fig. 1. Photograph and operational principle of an LSC based on a thin dye-doped polymer film. Incident light (blue arrows) is absorbed by the dyes inside of the zeolite L crystals and the re-emitted light is guided toward the edges by total internal reflection (yellow arrows).[2]

Our approach to these issues lies in using highly organized dye-zeolite composites with photonic antenna functions. The key idea is to minimize self-absorption by preparing multi-dye loaded zeolites where a Förster Resonance Energy Transfer cascade absorbs light over a large spectral range and transports the energy to a final acceptor emitting in the NIR range.

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[3] (a) Patent EP 1873202 B1, granted 11.02.2009; Patent US 7,655,300 B2, granted 02.02.2010; Patents pending in China, Japan, South Korea, India.(b) Luminescence concentrators and luminescence dispersers on the basis of oriented dye-zeolite antennas. patent CH-698333, granted 15.07.2009; pending WO 2010/009560 A1.

Functionalised Clathrochelate Complexes – New Building Blocks for New Supramolecular Structures

Matthew Wise, Kay Severin
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Ecole Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland
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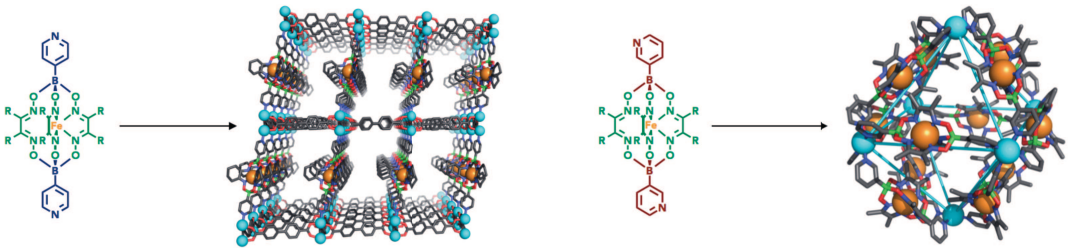
The structure and function of a supramolecular assembly is determined by the building blocks from which it is derived. Consequently, control over the steric, functional and geometric characteristics of these building blocks is an imperative aspect of supramolecular chemistry.[1] We have developed a new family of building blocks based upon boronic acid-capped tris(dioxime) iron(II) clathrochelate complexes and shown these complexes to be extremely versatile scaffolds for the preparation of long, rigid bipyridyl ligands. The length, steric bulk and co-ordination vectors of these metalloligands can be modulated simply by changing the simple starting materials from which they are synthesised. Clathrochelate-based metalloligands up to 5.4 nm in length and bearing 4-pyridyl groups were initially prepared, and the potential for these complexes as supramolecular building blocks was unveiled through their incorporation into a molecular square and a 3D coordination polymer.[2] Subsequently, clathrochelate complexes capped by 3-pyridyl groups, in combination with square planar Pd^{2+} ions, were employed in the preparation of octahedral cage compounds.[3] The structure-directing role played by the clathrochelate itself is instrumental in this remarkable self-assembly process and enables a single, entropically disfavoured, unprecedented structure to be obtained from an inherently unpredictable 3,3'-bipyridyl building block.



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[3] M. D. Wise, J. J. Holstein, P. Pattison, C. Besnard, E. Solari, R. Scopelliti, G. Bricogne and K. Severin, *Chem. Sci.*, **2015**, DOI: 10.1039/C4SC03046J.

Enzymatic C-H bond cleavage probed by deuterium kinetic isotope effects

Pascal D. Engi, Matthias Knop, Florian P. Seebeck

Department of Organic Chemistry, St. Johanns Ring 19, 4056 Basel, Switzerland

C-H bond activation is often a key step in the synthesis of complex molecules, be it in biosynthesis or in lab-based synthetic organic chemistry and accomplishing these important chemical transformations with small molecular entities remains a challenge. There is a great interest in new methodologies, since functionalization of complex hydrocarbon scaffolds is something that synthetic chemists do on a daily basis. The problem of selectivity and the unreactive nature of these bonds, due to the high bond strength, pose constant obstacles in the design of new reactions. Small molecule catalysts rely on metalloorganic complexes in order to achieve selective C-H bond cleavage. In the realm of nature, enzymes are very efficient at catalyzing such reactions with the help of suitable cofactors, which can either be metallic such as an iron-heme complex, or non-metallic such as an SAM radical. We study C-H bond activation by an enzyme which catalyzes such a reaction on a methylene group without the apparent need of any metallic or non-metallic cofactors. Kinetic isotope effects measured with enantioselectively deuterated peptide substrates show that C-H bond cleavage is the rate limiting step in this reaction, which is efficient as well as highly stereoselective.

Plenary Lecture, Talk

The formation of silver nanoparticles via peptides

Sonja Kracht[1], Bernd Giese[1], Katharina M. Fromm[2] *

[1]University of Fribourg, [2]Katharina M. Fromm

Recently it was shown that peptides, dependent on their containing amino acids, play a role in the formation and stabilization of silver nanoparticles (AgNPs).[1] With the tetrapeptide Ac-(L)His-(L)Pro-Aib-(L)Tyr-NH_2 as a model system which carries histidine as silver-binding amino acid and tyrosine as source for electrons, generated by irradiation, we investigated the mechanism of the AgNP formation. Surprisingly, silver ions cannot be reduced to AgNP.

But in the presence of chloride ions or some presynthesized AgNPs the formation of AgNPs occurs upon irradiation. An explanation for this phenomenon is given by the different redox potentials of bulk (E^0 = 0.8 V) and atomic silver (E^0 = -1.8 V). Only in the case of bulk silver the AgNP formation becomes exergonic and therefor favored. Using tyrosine as an electron source leads to the necessity of a long distance electron transfer before the silver ion can be reduced to Ag^0 either wise.

In the presence of chloride the size distribution of the AgNPs as well as the velocity of the AgNP formation is highly influenced by the chloride concentration, pH and irradiation wavelength; lower chloride concentrations and higher pH values lead to the generation of bigger nanoparticles which partly undergo a transformation upon irradiation into smaller nanoparticles, nicely shown by the appearance of an isosbestic point in the UV-vis spectra.

Clarifying the mechanism, the role of the main players in this process of AgNP formation and the break-up of the particles will give us a deeper understanding in the interactions and reactions of biomolecules with metal ions.

[1] "Silver Nanoparticle Formation in Different Sizes Induced by Peptides Identified within Split-and-Mix Libraries", Belser, K.; Vig-Slenters, T.; Pfumbidzai, C.; Upert, G.; Mirolo, L.; Fromm, K. M.; Wennemers, H., *Angew. Chem. Int. Ed.* **2009**, *48*, 3661.

Catalytic Strategies for Nucleic Acid Tagging

Kiril Tishinov, Dennis G. Gillingham

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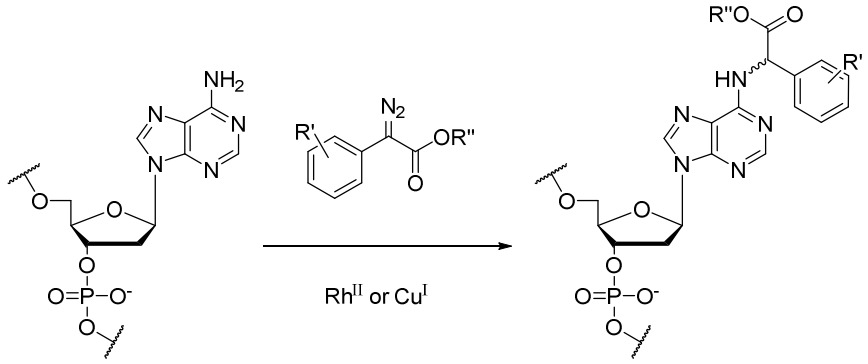
The field of nucleic acid research heavily relies on strategies for DNA and RNA tailoring in order to label them, or expand their functional potential. The development of such methodologies is a key step not only to the complete understanding of their biological role, but also to directly perturb their function for diagnostic and therapeutic use.



We have shown that a variety of nucleic acids can be catalytically alkylated with rhodium(II) and copper(I)-carbenoids generated from α-diazo carbonyl compounds. The alkylation takes place via an N-H insertion reaction selectively targeting the nucleobases in single-stranded DNA and RNA motifs [1,2]. The use of alkyne-functionalized α-diazo carbonyl compounds allows tagging of the nucleic acid substrate with a wide range of reporter groups such as fluorophores and affinity tags via 'click' chemistry.

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[2] K. Tishinov, N. Fei, D. G. Gillingham, *Chem. Sci.* **2013**, *4*, 4401.

Plenary Lecture, Talk

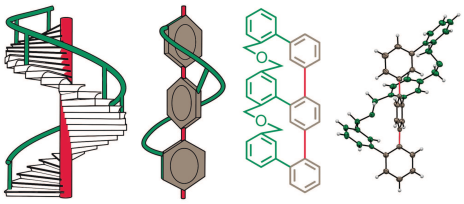
Dance Pairs - Inducing and Distorting Helicity in Achiral Polycyclic Systems

Michel Rickhaus[1], Marcel Mayor[2] *

[1]University of Basel, [2]Marcel Mayor

Here we like to report a novel concept how to introduce helicity to an originally flat system[1]: By assembling a ladder structure and extending one of the rails with respect to the other, a twist is introduced. The resulting structures resemble a pirouetting dance ribbon or the bannister of a helical staircase.

Compared to the previously known bannister-oligomers as described by Vögtle and coworkers, our systems interlink three terphenyl rings by one bridge (instead of two) and thus lack a point of inversion. As a result, they exist exclusively as enantiomers. The heteroatoms in the bridge allow to fine-tune the properties.



The systems was accessed over 12 steps and were fully characterized. X-Ray diffraction revealed indeed helical structures as envisaged. The obtained high racemization barrier allowed us to separate and isolate the enantiomers by chiral HPLC, and subsequently study the racemization behavior in detail. Changing the heteroatoms in the bridge allowed to extend the twist and to compare racemization behaviors. We also designed a system with a structural defect that causes a less ideal twist, which led to significantly altered physical properties.

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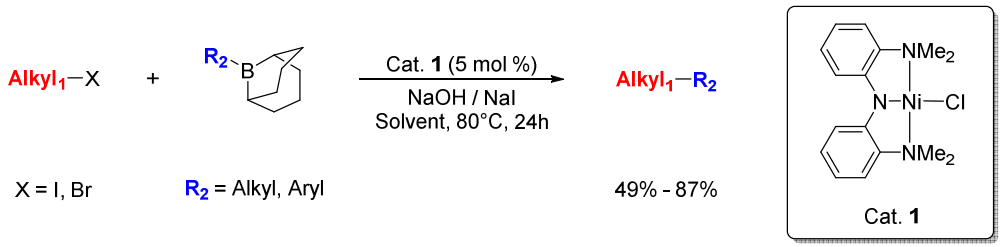
Suzuki–Miyaura Cross-Coupling Reactions of Unactivated Alkyl Halides Catalyzed by a Nickel Pincer Complex

Thomas Di Franco, prof. Xile Hu, LSCI, EPF Lausanne

The *Laboratory of Inorganic Synthesis and Catalysis* has developed a Nickel(II) complex with an amidobis(amine) pincer ligand, [($^{Me}N_2N$)Ni-Cl], which has shown a high efficiency in Kumada-Corriu-Tamao coupling and C-H functionalization reactions using unactivated alkyl halides as electrophiles. This complex affords a broad substrate scope and a high functional group tolerance. Due to the versatility of the [($^{Me}N_2N$)Ni-Cl] pincer complex, it is relevant to investigate its reactivity in the Suzuki-Miyaura reaction, which is one of the more powerful methods for the C-C bonds formation. It was found that this Nickel(II) pincer complex is able to catalyze the alkyl-alkyl and the alkyl-aryl Suzuki-Miyaura coupling reactions of unactivated alkyl halides with 9-alkyl-9-borabicyclo[3.3.1]nonane and 9-aryl-9-borabicyclo[3.3.1]nonane reagents, respectively, achieving modest to good yields. The developed system is effective enough for a wide range of alkyl bromides and iodides. The conditions tolerate a variety of useful functional groups including ester, nitrile, furan, pyrrole, and various protecting group.



Fluorine-Free Blue and Green Emitting Iridium(III) Complexes for Light Emitting Electrochemical Cells

Cathrin D. Ertl, Edwin C. Constable, Catherine E. Housecroft

Department of Chemistry, University of Basel, Spitalstrasse 51, 4056 Basel, Switzerland

Due to their excellent photophysical properties and easy colour tunability, iridium(III) complexes are very well suited for solid state lighting devices such as light emitting electrochemical cells (LEECs). Charged Ir(III) complexes containing two cyclometallating and one ancillary ligand already meet the requirement of mobile ions necessary for functional LEEC devices.

New 2-phenylpyridine based cyclometallating ligands containing methylsulfonyl groups in various positions of the phenyl ring have been synthesised. Heteroleptic Ir(III) complexes of these ligands (Figure 1) have been prepared in order to investigate the influence of the sulfur substituents on the photophysical properties of the complexes.

In combination with electron-rich ancillary ligands such as 2-(1H-pyrazol-1-yl)pyridine, significant shifts of the emission maxima into the green and even blue region were achieved. If the new complexes prove to be stable under LEEC conditions, sulfone functional groups will become promising alternatives to fluorine substituents in the pursuit of stable and efficient blue/green emitters based on cyclometallated Ir(III) complexes.

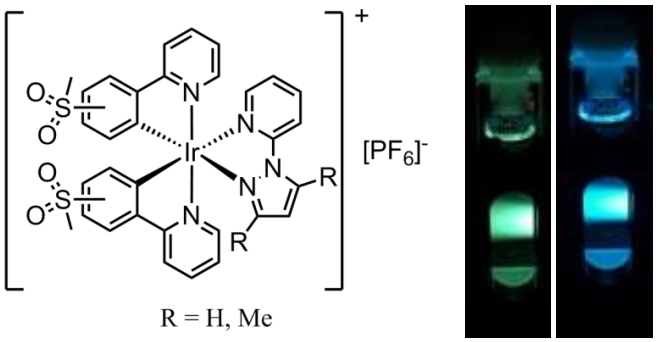


Figure 1. Chemical structure and emission colours of iridium complexes.

[1] Edwin C. Constable, Cathrin D. Ertl, Catherine E. Housecroft, Jennifer A. Zampese, *Dalton Trans.* **2014**, 43, 5343.

ANIONIC IR(III) COMPLEXES FOR LIGHT-EMITTING ELECTROCHEMICAL CELLS

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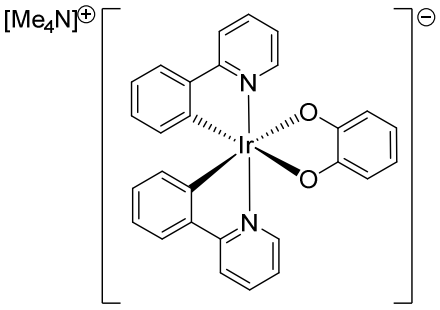
ABSTRACT

With roughly 20% of the world's total energy consumption attributed to lighting, more efficient devices are highly sought after and the subject of intense research efforts [1]. Significant progress has been made in the area of solid-state lighting with advances in light-emitting diodes (LEDs) and organic light-emitting diodes (OLEDs), however the high cost currently associated with producing multilayer OLED devices imposes limits on their widespread use. Light-emitting electrochemical cells (LECs) have emerged as an attractive option for solid-state lighting [2]. The simple design and ability to solution deposit the emissive layer of LEC devices without strict requirements on their encapsulation are highly advantageous in large-scale fabrication. Inorganic transition metal complex LECs are comprised primarily of cationic bis-cyclometallated Ir(III) complexes with a neutral N^N ancillary ligand. Anionic Ir complexes have been investigated to a much lesser degree but the few reported examples containing monodentate cyanide and thiocyanate ligands have shown promising photophysical properties [3,4]. We have investigated the use of catechol as a bidentate ligand for an anionic Ir(III) complex. The synthesis and characterization of the complex along with a detailed study of its redox behavior using EPR spectroscopy and spectroelectrochemistry are presented.



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Studies on the Chemistry and Biology of Fragin

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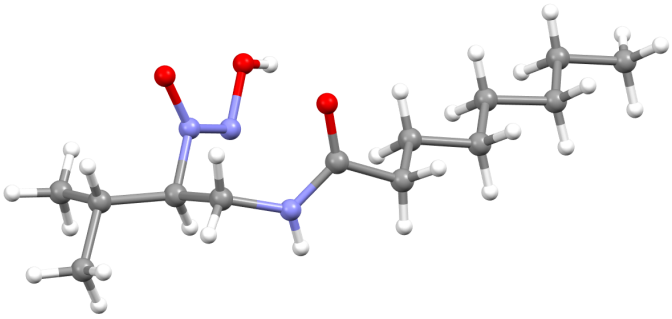
Fragin was isolated from *Pseudomonas fragi* in 1967[1] and its constitution was established by total synthesis[2] and X-ray crystallography.[3] To date, its absolute configuration has not yet been established. The natural product possesses an unusual *N*-nitroso-*N*-hydroxylamine functional group, which is present only in few natural products, and exhibits a range of biological activities such as growth inhibitor of algae and lettuce seeds, antifungal, antimicrobial and anticancer properties.[4]



Fragin

In this communication, we report our studies on the chemical and biological properties of this natural product.

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Organic Chemistry

Towards the Total Synthesis of Fidaxomicin

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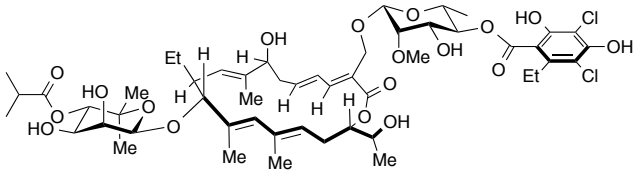
Fidaxomicin is a FDA-approved narrow spectrum antibiotic and currently used for the treatment of *Clostridium difficile* infections. This macrolide has also been found to exhibit potent biological activity against the multi-drug resistant *Mycobacterium tuberculosis*, however its poor pharmakokinetics prohibit its use as a drug.[1] Surprisingly, in spite of its significant biological properties and unique molecular structure no total synthesis of fidaxomicin has ever been reported since the first isolation in 1975.[2]



fidaxomicin

The total synthesis of this challenging 18-membered macrolide should pave the way to generate structurally diverse analogs and could provide new insights into the structure-activity relationship. After our successfull synthesis of the core aglycone[3], we are currently investigating the preparation of the carbohydrates and the challenging glycosylations to accomplish the total synthesis of fidaxomicin.

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_N_-Heterocyclic Carbene-Copper(I) Complexes as Catlysts for Direct Nucleic Acid Modification in Aqueous Media

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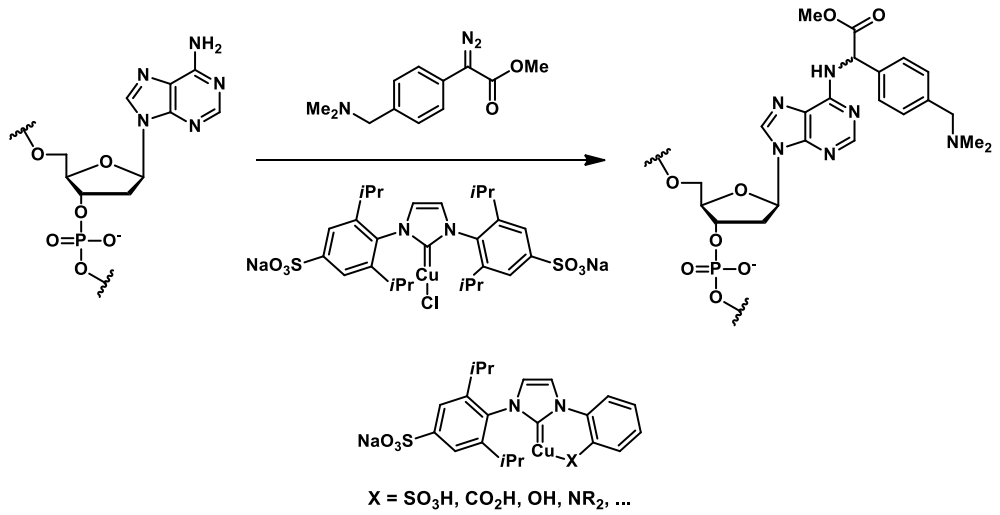
In the field of nucleic acid research methods for DNA and RNA modification are important tools to study their varied functions. In this sense the selective chemical manipulation of nucleic acids is crucial for better understanding and controlling their impact in biology.



Previous work from our group showed that nucleic acids can be catalytically modified with copper(I)-carbenoids generated from α-diazocarbonyl compounds [1]. The single stranded DNA and RNA motifs are alkylated via N-H insertion reaction selectively targeting the nucleobases. To overcome the oxidative damage which resulted from in-situ reduced Cu(II)SO_4, a water soluble NHC-copper(I) complex was used as catalyst instead. Further, the behavior of chelating NHC ligands towards complex stability was studied.

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Characterization and substrate specificity of the sulfoxide synthase EgtB from the ergothioneine biosynthetic pathway

Kristina V. Goncharenko[1], Allegra Vit[2], Wulf Blankenfeldt[2] and Florian P. Seebeck[1]

[1]Department for Chemistry, University of Basel, St. Johanns-Ring 19, 4056, Basel, Switzerland

[2]Structure and Function of Proteins, Helmholtz Centre for Infection Research, Inhoffenstr. 7, 38124 Braunschweig, Universitäts str. 30, 95447 Bayreuth, Germany

Ergothioneine is a 2-thiohistidine derivative produced by a broad range of pathogenic and saprophytic microorganisms. It also occurs in high concentrations in plants and specific human tissues. Although this sulfur compound most likely functions as an antioxidant, its precise physiological roles are not known. Biosynthesis of ergothioneine is supported by the unusual non-heme iron (II) enzyme EgtB. This sulfoxide synthase catalyzes the oxygen-dependent insertion of a sulfur atom into the C_2–H bond on the imidazole ring of *N*-α-trimethyl-*L*-histidine. Based on a crystal structure of EgtB from *Mycobacterium thermoresistibile* we designed an EgtB variant with a 4000-fold changed substrate specificity profile. This new enzyme preferentially accepts *N*-glutaryl-*L*-cysteine rather than γ-glutamylcysteine as sulfur donor. In addition we found out that EgtB from various organisms display a different choice of substrates. While EgtB from *Mycobacterium thermoresistibile* accepts γ-glutamylcysteine, EgtB from *Kurpida tusciae* requires *L*-cysteine as the sulfur donor.

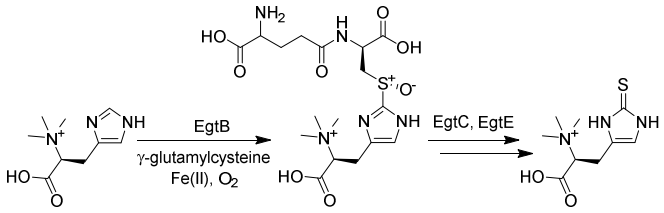


Figure 1. Biosynthesis of ergothioneine in *M. thermoresistible* via sulfoxide intermediate.

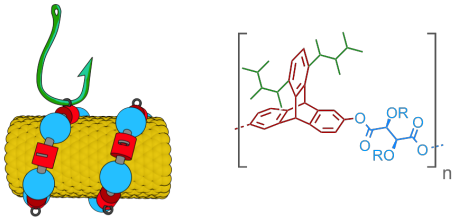
Plenary Lecture, Poster

Setting the Hook for Specific Single Walled Carbon Nanotubes (SWCNT)

Ina Bodoky[1], Marcel Mayor[2] *

[1]Basel, [2]Marcel Mayor

The desire to selectively address SWCNT with well-defined characteristics such as diameter, n,m-indices and even chirality, is an ongoing challenge in today´s research as the electronic properties of SWCNT depend strongly on these characteristics.[1][2][3][4]Here, we propose a strategy to achieve a controlled and selective separation of SWCNT depending on their size or possibly even their chiratily. The main idea consists on synthesizing an enantiomerically pure building block with a concave π-system using Diels-Alder reactions as key step. Polymerization with interlinking building blocks leads to a chiral ribbon, which is envisaged to coat selectively one type of SWCNT and disperse it. The driving force for the coating process is mainly the interaction of the SWCNT with the concave π-moiety and the size exclusion is essentially directed by the interlinking molecules and the structure of the polymer. Variation of the linkage allows altering of the properties of the polymer at a late stage in the assembly and ultimately defines the dispersion capability of the polymer. Finally, as an easy release of the coated SWCNT is highly desirable, we also propose a retroDiels-Alder-based release strategy.



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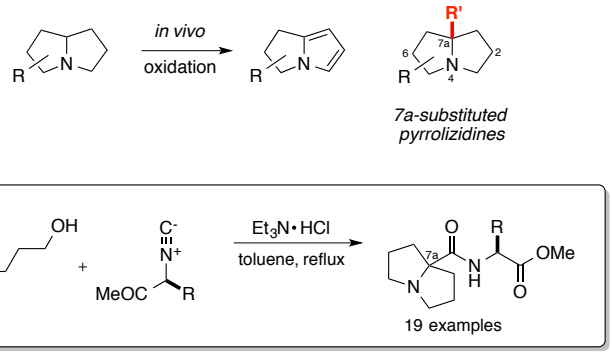
Direct Preparation of Pyrrolizidines Using Imines and Isonitriles

I. P. Kerschgens, K. Gademann

Department of Chemistry, University of Basel, St. Johanns-Ring 19, 4056 Basel, Switzerland

Pyrrolizidines constitute a privileged ring structure in alkaloids, with hundreds of natural products employing this motif.[1] The utilization of these bicyclic N–heterocycles in drug discovery has been hampered by their well-known *in vivo* oxidation to the corresponding pyrrole derivatives, which can undergo undesired off-target reactions.[2] One way of preventing this aromatization involves quaternization by the presence of an additional substituent on the 7a-position. Interestingly, among the many approaches to these heterocycles, there are only few methods reported in the literature to prepare these 7a-substituted pyrrolizidine carboxamides.[3] We describe an acid mediated annulation reaction for the direct preparation of 7a-substituted unnatural pyrrolizidines. A hydroxy-functionalized pyrroline is reacted with a large variety of isonitriles directly resulting in the target compounds. The reaction is operationally simple and tolerates air and water and the resulting pyrrolizidines can be further transformed to the corresponding oxidized and reduced derivatives. Preliminary mechanistic studies were performed to understand this unusual cyclization reaction.



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PEG-PCL block copolymers: new insights into the well-known synthesis

Amphiphilic block copolymers are becoming more and more attractive in the field of drug delivery research due to their mechanical and chemical stability compared to liposomes. In addition, copolymers provide different possibilities in terms of chemical structure.

Polyethylene glycol (PEG) is biocompatible hydrophilic polymer. Polycaprolactone (PCL) is a hydrophobic biodegradable polymer. Chemical combination of these two polymers leads to formation of various copolymers with a potential application as drug delivery systems. For example, depending on the hydrophilic (PEG) to hydrophobic (PCL) ratio, PEG-block-PCL copolymers form micelles, vesicles, and elongated structures [1].

Synthesis of such block copolymers is well-described in literature. In general, PEG together with a catalyst initiates ring-opening polymerization of ε-caprolactone (ε-CL). $Sn(Oct)_2$ is the most applied catalyst for this process. The mechanism of polymerization of ε-CL on butyl alcohol with $Sn(Oct)_2$ catalyst has been studied by A. Kowalsky et al. [2]. They showed that tin(II) alkoxide, formed in reversible reaction between alcohol and $Sn(Oct)_2$, acted as an actual initiator. Moreover, after polymerization BuO-PCL-OSnOct species were detected [3].

In this work, we studied polymerization of ε-CL on PEG with $Sn(Oct)_2$ catalyst. In contrast to previous studies, we observed a high-molecular weight shoulder corresponding to PEG-PCL-O-Sn-O-PCL-PEG species. In principle, copolymer-tin(II) bond could be cleaved by acid. However, we observed that PCL block degrades under these conditions. We also found that PEG-PCL-OSnOct affects further tosylation step: we were not able to obtain PEG-PCL-OTs. Meanwhile, tosylation of commercially available PEG or PCL normally proceeds smoothly. In this presentation, we discuss possible mechanism of cleavage of tosyl group, ways to overcome it, and strategies to avoid formation of PEG-PCL-O-Sn-O-PCL-PEG species.

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GREASY TAILS SWITCH 1D-COORDINATION $[ZN_2(OAC)_4(4,2':6',4''\text{-TPY})]_N$ POLYMERS TO DISCRETE $[ZN_2(OAC)_4(4,2':6',4''\text{-TPY})_2]$ COMPLEXES

Y. MAXIMILIAN KLEIN (1), JENNIFER A. ZAMPESE (1) AND CATHERINE E. HOUSECROFT (1)
(1): Department of Chemistry, University of Basel, Spitalstrasse 51, CH-4056 Basel, Switzerland

ABSTRACT

Coordination polymers of $Zn(OAc)_2$ with 4' substituted 4,2':6',4''-terpyridines (4,2':6',4''-tpy) have been reported in literature and normally 1-D polymer chain are obtained[1]. Ligand 4'-(4-dodecyloxyphenyl)-4,2':6',4''-tpy (**1**) has a long alkoxy chain and with $Zn(OAc)_2$ a discrete complex is obtained[2]. For a proper investigation of this change in assembly, ten complexes of $Zn(OAc)_2$ with 4'-(4-alkoxyphenyl)-4,2':6',4''-terpyridines from methoxy to decoxy have been synthesized. Their packing interactions have been investigated by X-ray diffraction and compared with the structure of $[Zn_2(OAc)_4(\mathbf{1})]$. Six have grown as one dimensional coordination polymers and 4 discrete complexes have been obtained. A change from polymer to discrete complex occurs between $[Zn_2(OAc)_4(\mathbf{2})]$ (Figure 1b) and $[Zn_2(OAc)_4(\mathbf{3})]$ (Figure 1c) and explanations for this phenomenon are given in this work[3].

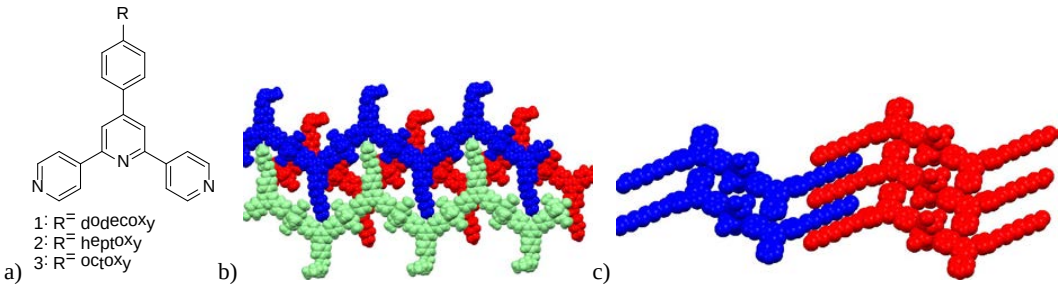

Figure 1: a) 4' substituted 4,2':6',4''-terpyridines. b) Coordination polymer arrangement in $[Zn_2(OAc)_4(\mathbf{2})]$. c) Assembly of the discrete complex $[Zn_2(OAc)_4(\mathbf{3})]$.

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Cascade Reactions enable by Regeneration of an NADH Mimic by an Artificial Metalloenzyme

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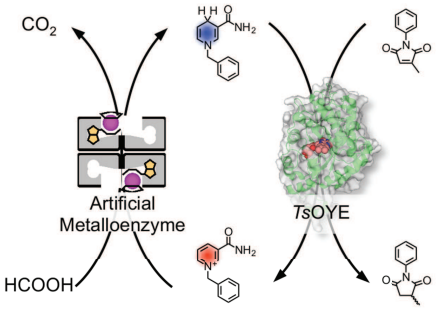
Nicotinamide adenine dinucleotide (NADH) is one of the major cofactors in biotransformations. Efficient methods for NADH regeneration with cheap reducing agents have been developed for catalytic use of expensive NADH.[1] To lower the cost of NADH, synthetic and functional NADH mimics have been utilized for several NADH dependent enzyme.[2,3] These NADH mimics are readily accessible and cheap. Furthermore, they improve the activity of some NADH-dependent enzyme. Although alcohol dehydrogenases are widely used for NADH regeneration, it does not work efficiently for the regeneration of NADH mimics.[2] Here we demonstrate the regeneration of an NADH mimic using an artificial metalloenzyme comprised of a streptavidin host and a biotinylated Iridium catalyst. As a protein matrix, streptavidin compartmentalizes the abiotic cofactor thus preventing mutual inactivation between the precious metal and the NADH dependent enzyme. Genetic optimization of streptavidin allows to significantly increase the NAD-regeneration rate. To illustrate the validity of the approach, we present a cascade reaction resulting from the combination of the artificial metalloenzyme and an old yellow enzyme from *Thermus scotoductus* (*Ts*OYE) (See Scheme)



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Poster, Poster

Chaperonin-polymer conjugates synthesized by atom transfer radical polymerization (ATRP) for siRNA encapsulation and release

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The chaperonin thermosome (THS) from *Thermoplasma acidophilum* is a spherical hexadecameric protein complex with a diameter of approx. 16 nm. Each hemisphere is composed of alternating α- β- subunits with a molecular weight or around 58kDa. THS encloses two cavities with a void volume of around 130nm^3.[1] The special feature of THS is that it possesses two large gated pores, which allow macromolecules like proteins [2] or polymers [3] to enter and leave the cavities. A genetically modified variant of THS was used, which had one accessible cysteine on the interior of each β-subunit.[2b] This allowed attachment of ATRP-initiators to the cysteines in order to perform controlled radical polymerization within the cavities by a grafting-from approach under ARGET ATRP conditions. 2-(Dimethylamino)ethyl methacrylate (DMAEMA) was used as monomer, which has tertiary amine groups that can be positively charged. The anionic oligonucleotide siRNA was then entrapped within the cavities via ionic interactions with the linear poly(DMAEMA) chains. The THS-poly(DMAEMA) construct protected the RNA from degradation by RNAses. Furthermore, the protein cage shields the cationic charges of poly(DMAEMA), which reduces the toxicity of the polymer. On-going experiments aim to deliver siRNA to cells by the THS-poly(DMAEMA) conjugate.

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Improving the Activity of Artificial Metalloenzymes Based on the Biotin-Streptavidin Technology

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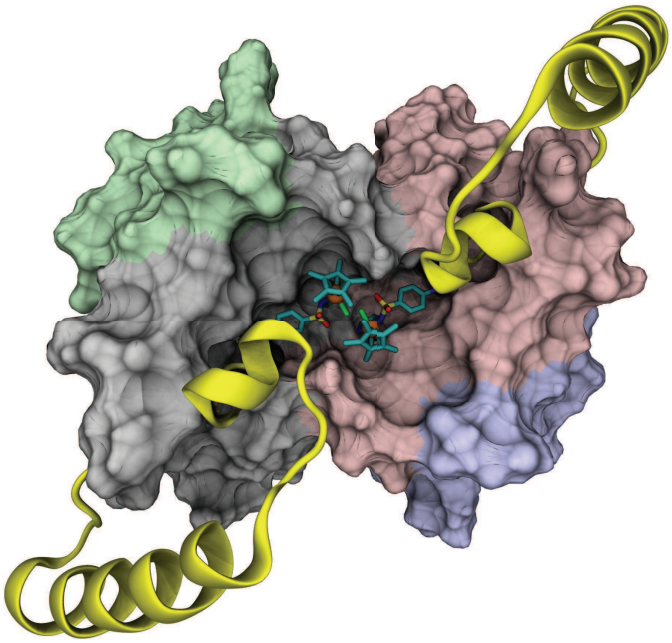
Artificial metalloenzymes (ArMs), the combination of an organometallic catalyst precursor with a host protein, offer new opportunities in biocatalysis.[1] By genetic modification of the host protein, the second coordination sphere around the metal can be fine-tuned, thus allowing to improve the scope and the performance of ArMs. As we have recently shown, the catalytic efficiency of an artificial imine reductase could be 8-fold improved by introduction of lipophilic point mutations around the active site.[2] Hence, the introduction of enlarged motifs such as loops or α-helices at selected positions around the active site might lead to further improvement of the performance of ArMs (Fig: Streptavidin-Ir(III)complex[3] with α-helix motif (yellow), hypothetical structure based on PDB ID 3PK2). By partly closing the binding site vestibule, a very different reaction environment can be created (e.g. a mainly apolar one favouring lipophilic substrates). Additionally, the active complex might be better shielded against catalyst inhibitors (e.g. glutathione). Therefore catalysis in complex media may be achieved, thus potentially allowing to perform catalysis in cell free extracts or even *in vivo*.



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Poster, Poster

Peptidic nano-carrier for drug and gene delivery

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The research and development of nano carrier systems is an emerging field in Nano medicine. In order to deliver fragile and insoluble drugs and/or therapeutic nucleic acids, sophisticated delivery systems are necessary. Peptides serve as promising candidates not only due to their defined and monodisperse character but also because of the unique possibility for specific functionalization through single changes in the peptidic sequence. This leads to a wide array of self-assemblies.[1]

Short amphiphilic peptides were designed using hydrophobic blocks inspired from gramicidin A. With various hydrophilic blocks, the assembly behavior was tunable obtaining structures from micelles, fibers, and vesicles to multi compartment micelles, termed peptides beads.[2] Encapsulation of hydrophilic and hydrophobic payloads, siRNA and plasmid DNA confirmed their potential as drug carrier. Preliminary studies showed responsiveness to pH and to reduction potential due to incorporated release mechanisms as well as promising results for transfection with plasmid DNA and gene silencing.

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Solvation of formic acid in water and in organic solvents

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The massive and irresponsible exploitation of fossil fuels by mankind has detrimental effects on the whole ecosystem earth.[1] The inconvenient truth is that we have to address this problem sooner rather than later to avoid permanent damage for future generations. Hydrogen will play a crucial role in the forthcoming technological changes.[2-4] It cannot be used as a primary energy source, since there are only trace amounts of the elemental hydrogen in nature[5], but its advantages as an energy vector are very promising[6]: It is non-toxic, it can be easily produced from various sources on-site, using alternative energies, and finally, it can be transformed into other kinds of energy, without harmful side-effects on the environment.[7] However, transport and storage are still problematic.[8] Our idea is to store hydrogen chemically bound to small molecules in a way that allows a quick hydrogen evolution or storage on demand.[9] CO_2 has been proven to be a suitable carrier molecule for hydrogen, by forming formic acid. Beside the catalyst and the carrier substance, the solvent system plays a crucial role in this process.[10] It mediates the interactions between the reactants, catalyst, and the products. For this purpose, we examined the interactions of formic acid with some carefully selected organic solvents in greater detail, using NMR spectroscopy and calorimetric methods.

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