SCS
Swiss Chemical
Society

Swiss Young
Chemists' Association

14th Swiss Snow Symposium

for young Chemists

Book of Abstracts

January 22–24, 2016

Hotel Alphubel
Saas-Fee, VS

Welcome to the 14th Swiss Snow Symposium

Dear participants,

On behalf of the organizing committee, it is my pleasure to welcome you to the 14th Swiss Snow Symposium in Saas-Fee.

We are honored to announce that the 14th 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 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).

Along with the other members of the SYCA, I would like to extend a very warm welcome to the four invited speakers: Prof. Stefan Willitsch, Dr. James W. Walton, Dr. Cédric Invernizzi, Dr. Basile F. E. Curchod, and to the generous sponsors whose kind contributions enable this event to take place.

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

Best wishes,

Cornel Fink
President, SYCA

We gratefully thank our sponsors

ACTELION

MERCK

SHIMADZU
Excellence in Science

MDPI
OPEN ACCESS

MLT AG
Labortechnik
Switzerland
Ihr Schweizer Laborunternehmen. Seit 1986.

KontaktGruppe für Forschungsfragen
Contact Group for Research Matters
BASF
The Chemical Company
NOVARTIS
Roche
syngenta

Table of Contents

- **Invited speakers**

- **Ph.D. talks**

Organizing Committee

Cornel Fink, President, SYCA
Sabine Malzkuhn, Vice-President, SYCA
Simone Grendelmeier, Treasurer, SYCA
Lucinda Kate Batchelor, Secretary, SYCA

Venue Address

Hotel Alphubel
CH-3906 Saas-Fee VS
Tel. +41 27 958 63 63

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 22nd

from 17.00	**Registration, Poster Installation, Apéro**
19.00-20.30	**Dinner**
20.30-21.30	**Invited Lecture: Prof. Stefan Willitsch, University of Basel** *“Cold Molecular Ions in Traps: From Precision Measurements on Single Molecules to the Control of Chemical Reactions”*
21.40-22.40	**Invited Lecture: Dr. Basile F. E. Curchod, Max Planck Institute** *"Towards In Silico Photochemistry"*
22.40-22.50	**Break**
22.50-00.10	**Session 1 (Chair: Cornel Fink and Lucinda Batchelor)**
22.50-23.10	Kristina V. Goncharenko, University of Basel
23.10-23.30	Hristo Varbanov, EPF Lausanne
23.30-23.50	Evgeny Smirnov, EPF Lausanne
23.50-00.10	Augustin A. S. Tchawou, ETH Zurich

Saturday, January 23rd

7.30-09.00	**Breakfast**
09.00-17-00	**Free Time**
17.15-18.15	**Invited Lecture: Dr. Cédric Invernizzi, Spiez Laboratory** *“Scientific Research and the Dual Use Problem”*
18.15-19.00	**Poster Session**
19.00-20.30	**Dinner**
20.45-21.45	**Invited Lecture: Dr. James W. Walton, University of Durham** *"Ruthenium Complexes for Catalysis and Therapy"*
21.45-22.00	**Break**
22.00-23.00	**Session 2 (Chair: Sabine Malzkuhn and Simone Grendelmeier)**
22.00-22.20	Andrea Pannwitz, University of Basel
22.20-22.40	Mathieu Marmier, EPF Lausanne
22.40-23.00	Nicolas Luisier, EPF Lausanne
23.00-23.15	**Best Oral Presentation and Best Poster Awards**

Sunday, January 24th

7.30-09.00	**Breakfast**
09.00-10.00	**Checkout**
From 10.00	**Departure**

14th Swiss Snow Symposium

SCS
Swiss Chemical
Society

Swiss Young
Chemists' Association

Cold Molecular Ions in Traps: From Precision Measurements on Single Molecules to the Control of Chemical Reactions

Prof. Dr. Stefan Willitsch
Departement Chemie, Universität Basel

The recent progress in the preparation of neutral molecules and ions at temperatures close to the absolute zero point has paved the way for a range of new research directions at the interface between chemistry and physics. Ensembles of cold, spatially localized ions in traps, often referred to as Coulomb crystals [1], are particularly attractive systems in this context in which it is possible to observe, manipulate and control single isolated particles under precisely controlled conditions.

In the presentation, we will give an overview over some applications of cold molecular ions with recent examples from our work. We will first highlight results on chemical reactions between neutrals and ions at temperatures of a few millikelvin to illustrate exotic chemical processes that occur close to the absolute zero point of the temperature scale [2]. Second, we will discuss how single isolated molecules can be controlled on the quantum level [3] which serves as a basis for molecular quantum technologies and precision measurements of molecular properties [4]. Finally, we will present a new method to control chemical reactions of complex molecules by isolating distinct molecular conformations in an electric field and inducing their reaction with a localized reaction target of Coulomb-crystallized ions [5]. The presentation will finish with an outlook on future developments.

[1] S. Willitsch, *Int. Rev. Phys. Chem.* **31,** 175 (2012)

[2] F.H.J. Hall et al., *Phys. Rev. Lett.* **107**, 243202 (2011); *Phys. Rev. Lett.* **109**, 233202 (2012)

[3] X. Tong et al., *Phys. Rev. Lett.* **105**, 143001 (2010)

[4] M. Germann et al., *Nature Phys.* **10**, 820 (2014)

[5] Y.-P. Chang et al., *Science* **342**, 98 (2013)

14th Swiss Snow Symposium

SCS
Swiss Chemical
Society

**Swiss Young
Chemists' Association**

Towards In Silico Photochemistry

Basile F. E. Curchod
Theory Department, Max Planck Institute of Microstructure Physics, Halle (Germany)

What happens to a molecule once it has absorbed UV or visible light? How does the molecule release or convert the extra-energy it just received? Answering these questions clearly goes beyond a pure theoretical curiosity, as photochemical and photophysical processes are central for numerous domains like energy conversion and storage, radiation damages in DNA, or atmospheric chemistry, to name a few.

In the past two decades, theoretical chemists have devoted a lot of effort to understanding and simulating the dynamics of photoexcited molecules.
A photoexcited molecule will presumably relax in different electronic states as a result of its nuclear motion. This means that the well-known Born-Oppenheimer approximation – which proposes to neglect the coupling between electronic and nuclear motion – is no longer valid, and so-called nonadiabatic effects must be considered. Interestingly, these nonadiabatic effects are not only important in light-triggered processes, but they will likely play a role as soon as the description of a given chemical process requires more than one electronic state, like in electron transfer mechanisms, for example. The loss of the Born-Oppenheimer approximation, however, poses an important number of questions and challenges for theoretical chemists.

The central goal of this presentation is to introduce the non-specialist to the main ideas and methods of theoretical and computational photochemistry. The usefulness of these techniques for chemistry – as well as the challenges in their application – will be highlighted by selected examples on the photochemistry of organic molecules.

14th Swiss Snow Symposium

SCS
Swiss Chemical
Society
Swiss Young
Chemists' Association

Scientific Research and the Dual Use Problem

Cédric Invernizzi
Spiez Laboratory, Switzerland

„Killer mousepox virus raises bioterror fears" (New Scientist, 10 January 2001). "Five easy mutations to make bird flu a lethal pandemic" (New Scientist, 21 September 2011). „'Home-brew' morphine from brewer's yeast now possible" (Reuters, 18 May 2015). What triggers such worrisome news headlines like these that find their way even into daily press every once in a while?

A closer look reveals that it is neither about rogue states' bio-chemical warfare programs or terrorists' capabilities, nor is it about illegal activities of organized crime. Rather it is about findings from academic research that have been published in scientific journals or presented at scientific meetings. In other words, some novel findings emanating from basic scientific research may not exclusively serve purposes that are beneficial to the advancement of society. In present or enhanced form, such findings may in fact bear the potential of misuse by state or non-state actors in order to harm humans, animals or plants, or their habitats. This duality is nowadays recognized as the dual use problem in research, best coined by the US American expression "Dual Use Research of Concern" (DURC).

On-going discussions in international security-themed fora acknowledge the complexity of the matter: Is a "risk-benefit" analysis in the conventional sense, e.g. as applied to issues of biosafety, feasible? And how best to balance security concerns against academic freedom? In the end it boils down to the fact that "not only the solution is unknown, but the problem itself is initially not well defined, and the values that ought to drive its investigation and the valid methods to do so are unknown, unclear or in dispute, as are the set of applicable theoretical models, the solution set, and the criteria for successful resolution" (doi: 10.3389/fpubh.2014.00074). Hence, this calls for a precautionary principle that starts with fostering a culture of responsible conduct in the sciences and raising awareness among researchers about the dual use problem.

14th Swiss Snow Symposium

SCS
Swiss Chemical
Society

Swiss Young
Chemists' Association

Ruthenium complexes for catalysis and therapy

James W. Walton
Department of Chemistry, Durham University, South Road, Durham

We have shown the first example of catalytic S_NAr of unactivated aryl chlorides (see Chem Commun 2015, p276). Experimental evidence indicates that our method proceeds via an η^6-coordination mechanism with yields up to 90%. The rate determining step of this reaction is exchange of the η6-boud product for arene starting material. We have designed and synthesised novel Ru complexes that accelerate the rate of arene exchange by up to 18X.

We have also developed a series of Ru arene complexes as potential anticancer agents. We have probed the aqueous behaviour of these complexes and compiled toxicity data. Finally, we have developed a series of histone deacetylase inhibitors. This series of compounds is effective in inhibiting proliferation of ovarian cancer cells. In some cases, the compounds are selective towards cancer cell over healthy cells, whilst selected compounds show thermoresponsiveness.

Plenary Lecture Talk

Conversion of a non-heme iron-dependent sulfoxide synthase into a thiol dioxygenase by a single point mutation

Kristina V. Goncharenko, Florian P. Seebeck*
Department of Chemistry, University Basel, Switzerland
St. Johanns-Ring 19, 4056 Basel, Switzerland
kristina.goncharenko@unibas.ch

Sulfoxide synthases EgtB form a class of non-heme iron enzymes, which catalyze oxygen-dependent sulfur-carbon bond formation between low molecular weight thiols and N-α-trimethylhistidine as the central step in ergothioneine biosynthesis. The crystal structure of EgtB from Mycobacterium thermoresistibile in complex with gamma-glutamylcysteine and N-α-trimethylhistidine implicate both substrates and three histidine residues as ligands in an octahedral iron binding site. In the secondary coordination sphere we identified a tyrosine residue which may serve as a hydrogen-bond or proton donor to an iron (III)-superoxo or - peroxo species. A single point mutation converts this enzyme into a γ-glutamylcysteine dioxygenase with efficiency that rivals naturally evolved thiol dioxygenases.

Plenary Lecture, Talk

New HTS-based approach in the quest for improved platinum-based chemotherapy of cancers with poor prognosis

Hristo P. Varbanov[a,b], Fabien Kuttler[b], Damiano Banfi[b], Paul J. Dyson[a]
[a] Institut des Sciences et Ingénierie Chimiques,[b] Biomolecular Screening Facility,
Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015, Lausanne, Switzerland
hristo.varbanov@epfl.ch

Cancer is a large group of diseases, featuring over 100 subtypes, which differ dramatically in terms of incidence, mortality and prevalence. The improvements in treatment strategies together with an earlier diagnosis have increased significantly the survival of cancer patients during the last four decades. Notably, the cure rate of patients, diagnosed with testicular cancer has increased from 10 to over 95% after the introduction of cisplatin; nowadays, cisplatin and its analogues are applied in nearly 50% of anticancer regimens.[1] Cancer types, which are not treated effectively with platinum-based drugs usually have poor prognosis with a ten-year survival of less than 10% (pancreatic and lung carcinoma).

In the quest for improving the therapy of tumors with high mortality, we have developed and validated a cell based HTS assay, searching for molecules which potentiate the activity of platinum-based drugs (i.e.: cisplatin, carboplatin and oxaliplatin) in PANC-1 (pancreatic carcinoma) and A549 (lung cancer) cell lines. The Prestwick Chemical Library® consisting of 1280 chemically and pharmacologically diverse small molecules, approved from the FDA, EMA and other regulating agencies provides a reasonable choice of candidates for this study. The potency of the library drugs alone and in combination with the platinum cytostatics against PANC-1 and A549 cells was assessed by means of the PrestoBlue fluorescent assay in 384-well plate format. More than 60 molecules showing cytotoxic activity against one or both cell lines were identified. The most active amongst them (e.g. anthracycline antibiotics, cardiac glycosides, etc.) showed scores over 0.9 (survival index < 0.1), indicating that most of the cells were dead at the conditions used. Most of the library hits maintained their activity in presence of the platinum drugs, while some showed a potential synergetic (i.e. more than just additive) effect.

The subsequent analysis (e.g. dose-response combination index[2] and fluorescent microscopy studies) of selected synergistic platinum-library drug combinations is presented. Furthermore, the promising combination is used as a base for the design and development of novel bifunctional platinum(IV) prodrugs.

Acknowledgements: H.V. is indebted for the financial support of FWF (Schrödinger fellowship J3577-B13).

Reference:

1. Wheate, N.J., Walker, S., Craig, G.E., Oun, R. (**2010**) The status of platinum anticancer drugs in the clinic and in clinical trials, Dalton Trans., *39*: 8113–8127.
2. Chou, T.C., (**2006**) Theoretical Basis, Experimental Design, and Computerized Simulation of Synergism and Antagonism in Drug Combination Studies, Pharmacol. Rev., *58*: 621-681.

Plenary Lecture, Talk

Optical Response of Self-Assembled Gold Nanofilms at Liquid|Liquid Interfaces: in situ study

E. Smirnov , P. Peljo , M. Scanlon[2], H. Girault *
EPF Lausanne, Switzerland
Av. F.-A. Forel 2, 1015 Lausanne, Switzerland,
[2]University College Cork

Nanooptics is an emerging field in nanotechnology, which combines nanosized objects and unique light-matter interactions at nanoscale. One of the most promising nanoobjects suitable for nanooptics are metal nanoparticles (NPs), which possess Localized Surface Plasmon Resonance (LSPR). And the most attractive strategy, which can bring a significant shift in the area of optics production (especially for filtering and mirroring applications), is based on large- scale self-assembly of metallic NPs with tunable optical response on various substrates and interfaces.[2]

Recently we have developed a novel, scalable and simple method to obtain highly stable continuous gold nanoparticle (AuNPs) films at various liquid|liquid interfaces (LLIs).[3] Formation of such nanofilms requires only vigorous shaking of aqueous phase containing AuNPs with tetrathiafulvalene solution inorganic phase. The method allows creating both sub- and multilayer self-healing films (Fig.1A), which possess unique optical properties due to particles alignment at the interface. In this work we investigate optical responses both extinction and reflection of nanofilms in situ with stepwise increasing of AuNPs concentration (Fig.1B). Obtained results are intriguing and indicate non-linear behavior of assemblies with accumulating AuNPs. We propose that this effect is caused by morphological changes occurred in the film settled at LLI: 2D closed-packed films transfers into 3D thick layer. It may be utilized for further development of liquid filters and mirrors, as well as serve as good platform for ambiphase Surface-Enhanced Raman Spectroscopy (SERS).

Plenary Lecture Talk

Mechanism-based design and optimization of a catalytic electrophilic cyclopropanation without diazomethane

Augustin A. S. Tchawou W., Mihai Raducan, and Peter Chen*
ETH Zürich, Switzerland
Vladimir-Prelog-Weg 2, 8093 Zürich, Switzerland

Iodomethyl boron compounds, either the trifluoroborate or a boronic ester, cyclopropanate electron-rich olefins and unprotected allylic alcohols with Pd catalysts according to a novel, designed catalytic cycle. Proposed intermediates in a "diverted Heck" mechanism are observed by means of spectroscopic studies, which together with reaction kinetics, permit a mechanism-based optimization of the yield, selectivity, and scope of the catalytic electrophilic cyclopropanation. The reaction with crystalline, air- stable, non-hygroscopic and less toxic reagents replaces the Simmons-Smith-type reactions, as well as cyclopropanation procedures that require the use of diazomethane.

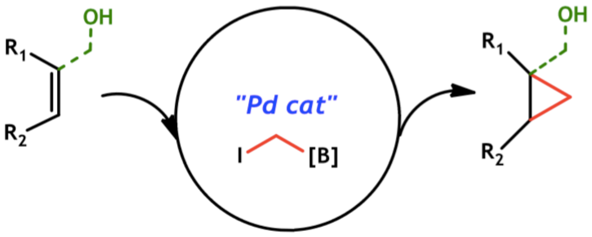


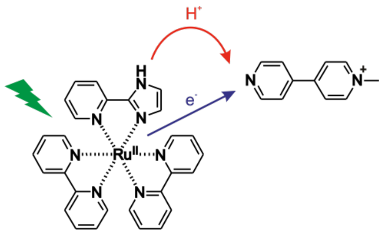
Figure: Iodomethyl boron as methylene transfer agent in a mechanism-based development of a Pd-catalyzed cyclopropanation of alkenes.

Plenary Lecture Talk

Light Driven Hydrogen Atom Release from a Ruthenium Complex

A. Pannwitz, O. S. Wenger*
Department of Chemistry, University Basel, Switzerland
St. Johanns-Ring 19, 4056 Basel, Switzerland
andrea.pannwitz@unibas.ch

Hydrogen atom transfer (HAT) is important in enzymes and in synthetic organic chemistry, for example for hydrogenations of unsaturated compounds such as ketones and imines. It would be attractive to use visible light as an energy resource to perform HAT reactions under mild reaction conditions. We therefore explored the (formal) HAT chemistry of photo-excited $[Ru(bpy)_2pyimH]^{2}$ (bpy 2,2'-bipyridine; pyimH 2-(2'-pyridyl)imidazole).^{,2} Upon photo-excitation into the long living ^{3}MLCT state, the formal bond dissociation free energy of the imidazole N-H bond drops by 50 kcal mol reaching a value comparable to typical ground state hydrogen atom donors on metal hydride basis.[3,4] Photo-induced formal HAT to monoquat (*N*-methyl-4,4'-bipyridinium) was investigated. Three different regimes for ^{3}MLCT quenching were observed depending on the pH of the solution.



---

[1] M A Haga, *Inorganica Chim. Acta* **1983**, *75*, 29

[2] K M ancaster, J B Gerken, A C Durre , J H Palmer, H B Gray, *Coord. Chem. Rev.* **2010**, *254*,1803

[3] M Bourrez, R Steinmetz, S Ott, F Gloaguen, Hammarström, *Nat. Chem.* **2015**, *7*, 140–145

[4] J Cho , M E Pulling, D M Smith, J R Norton, *J. Am. Chem. Soc.* **2008**, *130*, 4250–4252

Plenary Lecture Talk

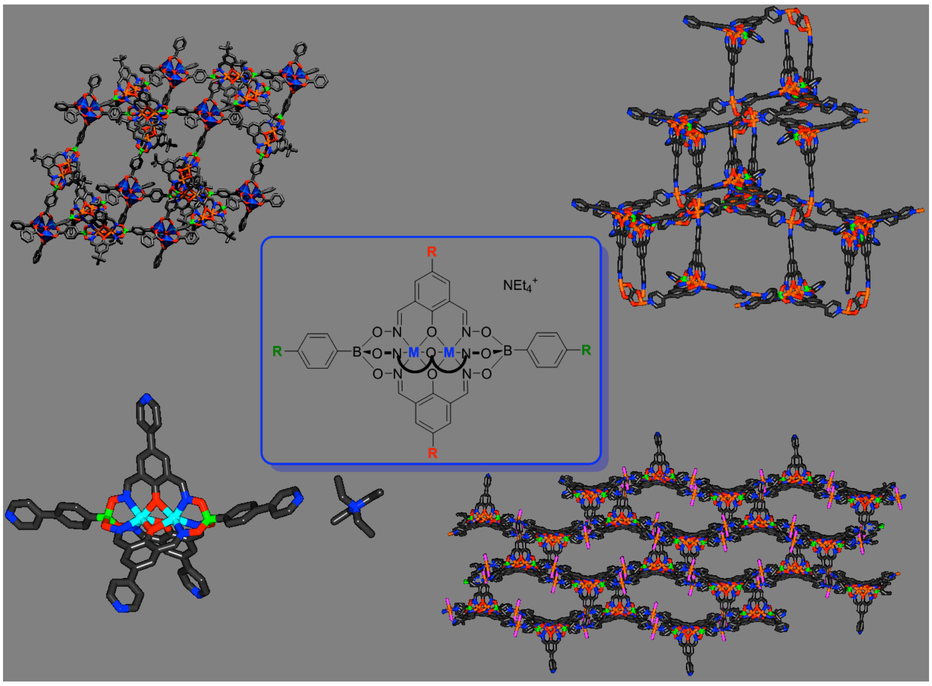
Polytopic Clathrochelates Ligands as Versatile Toolbox for Applications in Supramolecular Chemistry

Mathieu Marmier, Rosario Scopelliti, Kay Severin

Institut des Sciences et Ingénierie Chimiques, EPFL, 1015 Lausanne, Switzerland

mathieu.marmier@epfl.ch

A metalloligand is a metal complex appended with functional groups capable of binding to other metal ions. Compared to standard organic ligands, metalloligands have potential advantages: the internal metal ions can add novel functions such as redox-activity, color, magnetism, molecular recognition sites or catalytic activity. In addition, the metal ions can simplify the synthesis of the ligand if metal-templated reactions are employed. Metalloligands have been used extensively for the construction of molecular and polymeric nanostructures. We have recently described the synthesis of anionic metalloligands which feature functional groups appended to a dinuclear clathrochelate core containing either Zn^{2} or Co^{2} ions.[2] Exploring the reactivity and stability of these clathrochelates metalloligands, we have studied their incorporation in new supramolecular architectures displaying new properties, such as gas storage and luminescence, or coordination geometries (Figure 1).



Plenary Lecture, Talk

Crystalline and soft materials based on boronate esters and nitrogen donor ligands

N. Luisier, R. Scopelliti, K. Severin*

EPF Lausanne, Switzerland

Av. F.-A. Forel 2, 1015 Lausanne, Switzerland

nicolas.luisier@epfl.ch

It has been shown that dative boron-nitrogen bond between a Lewis basic N-donor atom and a Lewis acidic boronate ester can be efficiently used in structural supramolecular chemistry. Previous reports have shown its utilization for the formation of polymer materials or finite assemblies. We demonstrate here the use of this reversible covalent binding for the synthesis of a new class of organogel via B-N adducts formation of imidazolyl ligands on boronate ester compounds.[2] A large variety of boronate esters can be gelated together with bis(imidazole-1-yl)methane ligands in non-polar solvents such as 1,2-dichlorobenzene, toluene or mesitylene. Surprisingly gelation could also be achieved in polar solvents as THF or acetone. Some samples were showing very low critical gel concentration, as low as 0.02 percent in weight, which illustrate the strong binding of the gel components, and the large solvent-gelator interaction. We also reported the formation of a four-component organogel by*in-situ*synthesis of an imine-bridged diboronic acid through condensation of a formyl-benzeneboronic acid with an amino-benzeneboronic acid.[3] This last gel could successfully be post-modified to increase its mechanic resistance. We have also used boron-nitrogen interaction for the construction of crystalline 1-D polymers and macrocycle through rational design and synthesis of new pyridyl ligands.

Selected reviews: (a) Y. Kubo, R. Nishiyabu and T. D. James, *Chem. Commun*., **2015**, 51, 2005; (b) E. Sheepwash, B. Icli and K. Severin, *Chimia*, **2012**, 66, 212; (c) R. Nishiyabu, Y. Kubo, T. D. James and J. S. Fossey, *Chem. Commun.,* **2011**, 47, 1124; (d) K. Severin, *Dalton Trans.,* **2009**, 5254; (e) H. Höpfl*, Struct. Bonding*, **2002**, 103, 1.

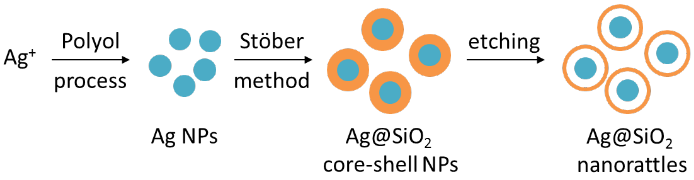
Design of $Ag@SiO_2$ nanorattles for antimicrobial implant coatings

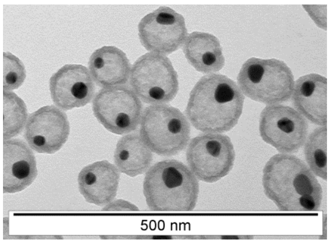
Sarah-Luise Abram, Katharina M. Fromm

University of Fribourg

Medical progress and an ageing world population have led to an increasing use of foreign materials inside the human body. Consequently also the number of infections related to these implants has grown significantly.[1] Antimicrobial coatings that prevent the formation of infectious biofilms on the surface of the implants could make an important contribution to overcome that issue. Silver is known for its good antimicrobial and biocompatible properties and could therefore play an important role in the fight against implant infections, especially if they are caused by antibiotic resistant bacteria.[2]

This project covers the synthesis of Ag nanoparticles that are encapsulated inside a protective silica shell in order to prevent aggregation or a too fast release of the antimicrobial active Ag^+ ions. The silica shell provides reactive sites to covalently attach the antimicrobial nanocontainers to the implant surface. Furthermore it enables the functionalization with biosensor units to create a stimuli responsive release of the Ag^+ only in the presence of bacteria.





We have developed a reliable synthesis of well-defined $Ag@SiO_2$ nanorattles that combines the polyol method for synthesizing Ag nanoparticles [3] with a modified Stöber method [4] for growing the silica shell and a surface protected etching protocol [5] for partial removal of the inner part of that shell.

[1] Suganthan Veerachamy, Tejasri Yarlagadda, Geetha Manivasagam and Prasad KDV Yarlagadda *Proc IMechE Part H: J Engineering in Medicine*, **2014**, 228, 1083-1099.

[2] Sonja Eckhardt, Priscilla S. Brunetto, Jacinthe Gagnon, Magdalena Priebe, Bernd Giese, Katharina M. Fromm, *Chem. Rev.*, **2013**, 113, 4708-4754.

[3] Pierre-Yves Silvert, Ronald Herrera-Urbina, Nicolas Duvauchelle, Venugopal Vijayakrishnan, Kamar Tekaia Elhsissen, *J. Mater. Chem.,* **1996**, 6, 573-577.

[4] Guo Liang Li, Chin An Tai, K. G. Neoh, E. T. Kang, Xinlin Yang, *Polym. Chem.,* **2011**, 2, 1368-1374.

[5] Feng Hu, Yan Zhang, Guangcun Chen, Chunyan Li, Qiangbin Wang, *small* **2015**, 11, 985-993.

Synthesis of metal oxide precursors for the generation of oxides or similar nanomaterials for Na-ion battery cathode production

Benoît Baichette*[1], Katharina M. Fromm[1]

*benoit.baichette@unifr.ch

[1]*University of Fribourg Department of Chemistry Fribourg Switzerland*

The current growing need of energy storage is an issue that can be solved at least partially by electrochemical storage, like batteries. Nowadays, most of the Li-ion battery cathodes are made of lithium cobalt oxide, $LiCoO_2$, prepared by highly energy consuming solid state processes, involving solid state method at high temperature and for long reaction times (600-900°C, 36hours[1]). Aurelien Crochet and Jean-Pierre Brog of the Fromm group developed a way of producing the high-temperature phase of LiCoO2 (HT-LiCoO2)[2] at low temperature using heterometallic Li-Co alkoxides complexes as molecular precursors, following the general equation below.

$$[Li_2Co(OR)_4(L)_4] \xrightarrow[\text{Ar, 2h}]{350\ 450°C} \text{HT-}LiCoO_2 + Li_2CO_3 + CO_2 + H_2O$$

Despite lower performances, Na-ion batteries are good candidates in an effort to produce cheaper and more environmentally friendly batteries compared to Li-ion batteries. Complexes of $[Na_xM_y(OR)_z(L)_a]$, where M is a transition metal, OR an alkyl or aryl oxide group and L a ligand, can be synthesized in analogy to the lithium precursors in order to use them for the generation of sodium metal oxides. Those oxides will be characterized and tested as cathode materials. We will present our first efforts and results on this kind of synthesis.

(1) Shao-Horn, Y.; Croguennec, L.; Delmas, C.; Nelson, E. C.; O Keefe, M. A. *Nat. Mater.* **2003**, *2*, 464–467.

(2) Brog, J.-P.; Crochet, A.; M. Fromm, K. Lithium metallary oxide clusters as starting products for oxide materials, January 5, 2012.

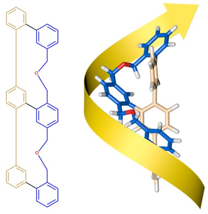
Plenary Lecture, Poster

Synthesis towards a new Diacetylene Bridged Geländer-Type Oligomer

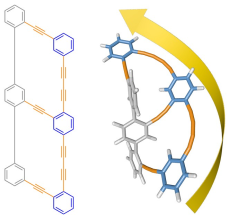
L. M. Bannwart[1], M. Mayor[1]*

[1]University of Basel

Atropisomers are chiral compounds that do not contain sterogenic centres, but a stereogenic axis. While the synthesis of chiral compounds containing chiral centres has been an important field of research for a long time, little was known about atropisomeric compounds, which were treated as an "academic curiosity". The interest in atropisomers started with the discovery that the configuration around a biphenyl axis is an important factor to control the pharmacological properties of bioactive compounds. Combined with their usefulness as catalysts in asymmetric synthesis, biphenyls became prominent and well-studied examples of "chiral compounds without stereogenic centre".



1



2

Vögtle et al[1] described a new class of bridged terphenyl compounds called geländer oligomers. In the classical geländer oligomers the optical inactive *meso* form is more stable than the pair of enantiomers. Recently, we reported a novel type of geländer oligomers that cannot exist as a *meso* form.[2],[3] However this benzyl ether-bridged molecule (**1**) has, the lowest barrier of racemisation measured so far. Therefore, we designed a new diacetylene-bridged molecule (**2**), which is expected to be more rigid. Consequently the racemisation process in this molecule should be significantly slower.

[1] Bernd Kiupel, Christoph Niederalt, Martin Nieger, Stefan Grimme, Fritz Vögtle, *Angew. Chem. Int. Ed.*, **1998**, 37, No. 21, 3031

[2] Michel Rickhaus, Linda Maria Bannwart, Markus Neuburger, Heiko Gsellinger, Kaspar Zimmermann, Daniel Häussinger, Marcel Mayor, *Angew. Chem. Int. Ed.,* **2014**, 53, 14587

[3] Michel Rickhaus, Oliver Unke, Rajesh Mannancherry, Linda Maria Bannwart, Markus Neuburger, Daniel Häussinger, Marcel Mayor, *Chem. Eur. J.,* **2015**, 21, 18156

Poster

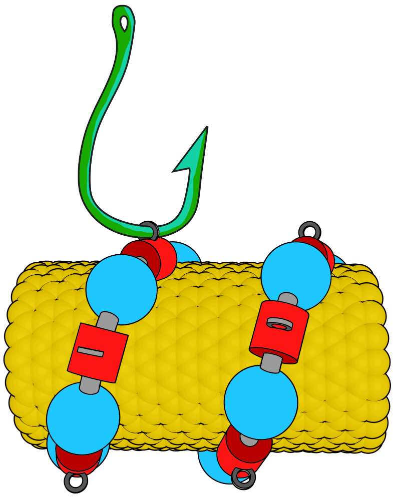
Synthesis of DMC from CO_2 using imidazolium based ionic-polymers

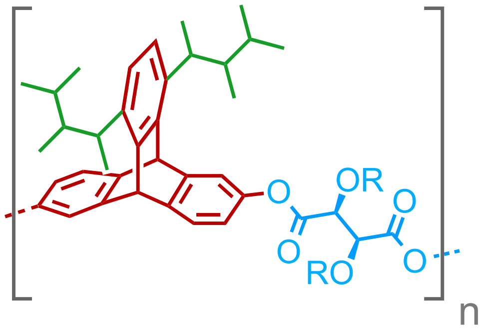
Carbon dioxide emissions are increasing every year, and have a direct impact on climate change. Manufacturing of products incorporating carbon dioxide is an efficient manner of adding-value to an anthropogenic waste. In particular, the cycloaddition of CO_2 to epoxides using imidazolium-based ionic liquids is an efficient and well-described process. Here, we synthesised and characterised a series of novel cross-linked imidazolium-based ionic polymers based on vinylbenzylimidazole and evaluated their activity in dimethycarbonate (DMC) production from CO_2 and epoxides. We found that the functional groups attached on the linkers are important for activity. Preliminary catalytic results show promising activity for a linker containing a diol unit.

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

Ina Bodoky and Marcel Mayor, Department of Organic Chemistry, University of Basel, St. Johanns-Ring 19, 4056 Basel, Switzerland

The desire to selectively address SWCNTs with well-defined characteristics such as diameter, n,m-indices and chirality, is an ongoing challenge in today´s research. Although the electronic properties of SWCNTs depend strongly on these characteristics[ ] [4], the selectivity towards traditional means of purification remains low at best. Here, we propose a new strategy to achieve a controlled and selective separation of SWCNTs depending on their size or very likely even their chirality. Conceptually this novel *hook* consists of an enantiomerically pure building block with a concave π-system, which can synthetically be accessed using Diels-Alder reactions as key steps. Polymerization with interlinking building blocks then leads to chiral ribbons, which are 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 while the size exclusion is defined by the interlinking molecules and the resulting secondary 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. As a reliable release of the coated SWCNT is highly desirable, we further present *retro*Diels-Alder-based uncoating strategies.





1

[ ] M Yu, B es, S A epa , R Ruoff, *Physical Review Letters*, **2000**, *84*, 5552-5555

[2] Q Cao, H K m, N mpa ka , J Ku ka , C Wa g, M S m, K Roy, M A A am, J A Roge s, *Nature*, **2008**, *454*, 495-500

[3] D D Tu e, B S ave , R K upke, J G S ap e , *Advanced Energy Materials.*, **2012**, *2*, 043- 055

[4] Z ao, Y -L & S odda , J , *Acc. Chem. Res.* **42,** 6 7 (2009) a d efe e ces e e

Chemical Biology, Poster

Bacterial Resistance to Silver: The Role of SilE Protein

Valentin Chabert, Katharina M. Fromm*

University of Fribourg

Silver has been used for hundreds of years for its antimicrobial properties. Since the emergence of many multi-resistant bacterial strains against classical antibiotics, the research of new silver compounds is now at its apogee. Nowadays, a lot of researches are focused on compounds with slow- and stimuli-responsive- release of Ag^+. While these drugs have been shown to be highly able to kill bacteria, some of these pathogens have developed a resistance to high concentrations of Ag^+.

This resistance is provided by the plasmid pMG101, which encodes for eight proteins that act together in an efflux pump system to deal with silver ions. Among these, the SilE protein is the only one of which its mode of action is actually unknown.

To identify the role of SilE in this bacterial machinery, two approaches have been intended in our group. While one way is to study the interaction of the whole protein with silver ions, the other is based on a bottom-up approach, investigating the interaction of silver ions with short peptide sequences of this protein.

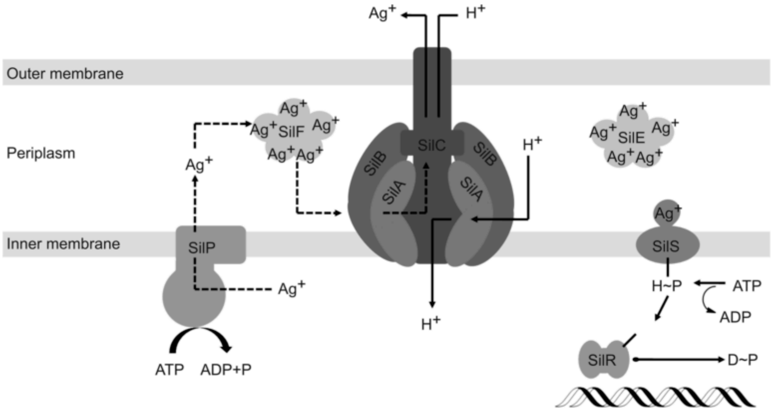


Figure 1: Proteins products of pMG101 silver resistance genes.

References:

S. Silver, L. T. Phung, G. Silver, *J. Ind. Microbiol. Biotechnol.* **2006**, 33, 627-634.

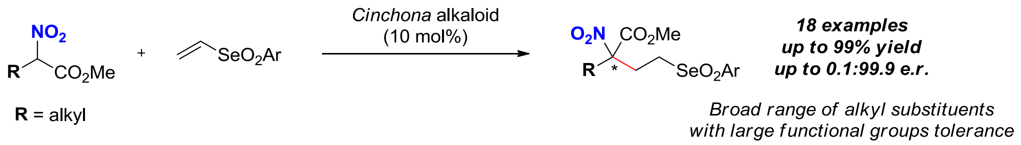
S. Eckhardt, P. S. Brunetto, J. Gagnon, M. Priebe, B. Giese, K. M. Fromm, *Chem. Rev.* **2013**, 113, 4708-4754.

Organocatalytic enantioselective Michael addition of α-alkyl substituted α-nitroacetates to phenyl vinyl selenone

Antonin Clemenceau, Qian Wang, Jieping Zhu*

Laboratory of Synthesis and Natural Products, Institute of Chemical Sciences and Engineering, Ecole Polytechnique Fédérale de Lausanne, EPFL-SB-ISIC-LSPN, BCH5304, CH-1015 Lausanne, Switzerland

Synthesis of enantio-enriched α-quaternary α-amino-acids has remained an active research area. We have recently described a *Cinchona* alkaloid-catalyzed Michael addition reaction of methyl α-aryl-α-isocyanoacetates to phenyl vinyl selenone. The resulting enantioenriched α-aryl-α-(2'-phenylselenonylethyl)-α-isocyanoacetates were subsequently converted into α-aryl-α-(2'-FG-alkyl)-α-amino acids and medicinally important heterocycles as well as natural product trigonoimine A.[1] To access α,α-dialkyl substituted α-amino acids, a novel *Cinchona* alkaloid-catalyzed enantioselective Michael addition reaction has been developed using α-alkyl substituted α-nitroacetates and phenyl vinyl selenone as reaction partners. Under optimized conditions, α-alkyl-α-(2'-phenylselenonylethyl)-α-nitroacetates were obtained in good to excellent yields and enantioselectivities. The broad substrate scope and the easy modification of the nitro and phenylselenonyl groups made this reaction a useful alternative for the synthesis of α,α-dialkyl substituted α-amino acids and other chiral building blocks.[2]



18 examples
up to 99% yield
up to 0.1:99.9 e.r.

Broad range of alkyl substituents with large functional groups tolerance

1. a) Buyck, T.; Wang, Q.; Zhu, J. *Angew. Chem. Int. Ed.* **2013**, *52*, 12714-12718; b) Buyck, T.; Wang, Q.; Zhu, J. *J. Am. Chem. Soc.* **2014**, *136*, 11524-11528.
2. Clemenceau, A.; Wang, Q.; Zhu, J. *manuscript in preparation.*

Plenary Lecture, Poster

Synergistic antimicrobial effect of silver and other metals in bimetallic complexes

P. C. Corcosa[1], K. M. Fromm[1]*

[1]University of Fribourg

The precious metal silver is aging for its excellent antimicrobial properties as throwing silver coins in fountains is not only a lovely old tradition.[1] It has been recognized to play an important role concerning medical applications, for example the coating of implants with Ag^0 or Ag^I coordination compounds to avoid infections due to bacterial biofilms formation.[2] The recent research of the FROMM group with respect to antimicrobial silver compounds was focused on silver coordination networks, meaning short PEG oligomers functionalized with (iso-)nicotinic acid as ligands. Thus, the aim of the project is to create new Ag^I complexes with bioinspired ligands, for example derivatives of phenylalanine, aminobenzoic acid or picolinic acid. Furthermore, we try to synthesize bimetallic complexes combining silver and another metal such as Zn or Cu with the ambition to generate synergistic antimicrobial effects and to elucidate structural characteristics.

[1] Fromm, K. M., *Nat. Chem.* **2011**, *3*, 178.
[2] Vig Slenters, T. et al. *Materials* **2010**, *3*, 3407-3429.

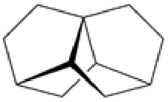
Plenary Lecture, Poster

Synthesis of a Tetracyclic Derivative of Norbornane

L. Delarue Bizzini[1], M. Mayor[1]*

[1]Universität Basel

One of the challenges of synthetic organic chemistry is structural diversity, in particular, at the level of small molecular building blocks.[1] New compounds and compound classes in the size range of small molecules (less than 500 g/mol) are of interest since they may display unforeseen properties and lead to new structural motifs.[2] The computer-assisted enumeration of the chemical space addresses this challenge by generating all possible molecules for a give number of atoms (excluding hydrogen) under consideration of specific rules.[3] One particular example found in the chemical universe database (GDB-11) is the yet unknown tetracyclic hydrocarbon **1**. This esthetically pleasing, *C*2-symmetrical, chiral molecule is comprised of three partially superposed norbornyl units. It is surprising that this unstrained molecule has not yet been synthesized in over 100 years of norbornane chemistry.[4] The goal of this project is to synthesize and study the properties of hydrocarbon **1**. Different strategies to build the tetracyclic scaffold will be discussed in the presentation.



1

[1] L. C. Blum, J.-L. Reymond, *J. Am. Chem. Soc.* **2009**, 131, 8732–8733.

[2] T. Fink, J.-L. Reymond, *J. Chem. Inf. Model.* **2007**, 47, 342–353.

[3] L. Ruddigkeit, R. van Deursen, L. C. Blum, Jean-Louis Reymond, *J. Chem. Inf. Model.* **2012**, 52, 2864-2875

[4] J.-L. Reymond, L. C Blum, R. van Deursen, *Chimia* **2011**, 65, 863-867.

Plenary Lecture, Poster

Application of ferrocene derivatives for stimuli-responsive polymers and for biosensor

M. Di Giannantonio[1], K. Fromm[1]*

[1]University of Fribourg

Since long time ferrocene and its derivatives have attracted the attention of the scientific and technical community because of its fascinating chemistry. Due to its easy functionalization and unusual and attractive properties, ferrocene derivatives have found different applications in material science, such as sensors, catalysts, polymers, electroactive materials and medicinal chemistry[1,2].

We propose two different research subjects: ferrocene-containing polymers as stimuli-responsive material and ferrocene-based trigger as biosensor.

The aim is to synthesize stimuli-responsive polymerswith several ferrocene units in a linear polyurethane chain or in a linear poly(methyl methacrylate) chain and to analyze their physico-chemical changessubjectingthe polymerto mechanical stress (sonication or stretching) or using techniques such as the Atomic Force Microscope.

Ferrocene derivatives can also be exploited for biomedical applications: the formation of resistant biofilms causes infection problems in the internal fixation devices[3]; the aim of this project is to synthesize an unsymmetrical ferrocene that could be a precursor of a new type of sensor for biomolecules, accounting for the presence of bacteria. Exploiting therotational freedom of ferrocene, temporally restricted by intramolecular-DNA near-match pairing and then quicklyreleased by hybridization with a fully-matching DNA strand, it is possible to identify the presence of bacteria.

[1] S. Zhai, J. Shang, D. Yang, S.Wang, J. Hu, G. Lu, X. Huang, *J. Polym. Sci. Part Polym.Chem.* **2012**, *50*, 811–820.

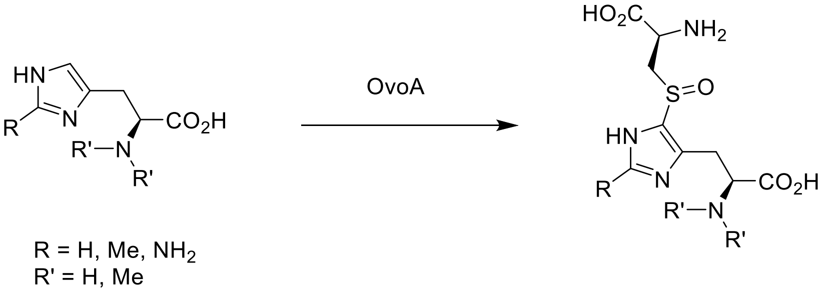
[2] C. Herfurth, D. Voll, J. Buller, J. Weiss, C. Barner-Kowollik, A. Laschewsky, *J. Polym. Sci. Part Polym.Chem.* **2012**, *50*, 108–118.

[3] *Science,* 8 February, **2002***: Vol. 295* no. 5557 p. 995.

Substrate specificity of an oxygen dependent sulfoxide synthase in ovothiol biosynthesis

Pascal Engi, Cangsong Liao, Gabriel T.M. Mashabela, Florian P. Seebeck

The sulfoxide synthase OvoA is a novel type of non-heme iron(II) enzyme that catalyzes the first step in ovothiol A biosynthesis. This enzyme is unrelated to any other type of non-heme iron(II) oxidases and catalyzes a reaction with no biological or chemical precedence. OvoA mediates O_2 dependent sulfur-carbon bond formation between imidazole side chain of L-histidine and the thiol side chain of L-cysteine. Enzymes which sulfurize non-activated hydrocarbons could open new avenues in the biotechnological production of complex molecules. In the present study we show that OvoA is characterized by a surprisingly broad substrate specificity, suggesting that this enzyme provides a promising starting point for enzyme design studies.



Plenary Lecture, Poster

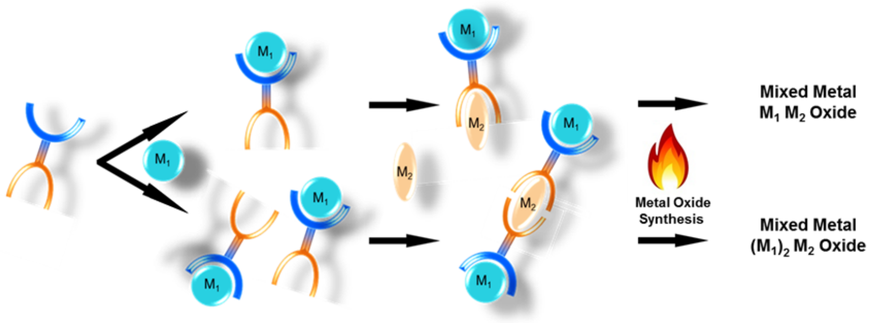
Multitopic precursors for oxide materials' synthesis

A. Finelli[1], A. Crochet[1], K. Fromm[1]*

[1]University of Fribourg

The research interest in mixed metal oxides is increasing in material science, as they have multiple applications, such as in batteries, ceramics, pigments, high-Tc superconductors or transparent conductors.

However, the two main challenges for the synthesis of such compounds are the lack of control on the ratio of the different metal components and the extreme conditions (up to 900 °C) that many of these oxides require during their traditional solid state synthesis.



To overcome these issues, we propose a strategy for the synthesis of mixed metal complexes, which is based on precursors of coordination compounds, using the "multitopic ligand approach".

The aim is to design specific ligands with selective coordination sites to bind different metal ions. Due to the metal ion preorganization in the precursor thus formed, the stoichiometry of the final oxide material can be controlled and the extreme synthesis conditions diminished (pressure or temperature).

These new mixed metal complexes will be finally combusted to oxide materials with possible new features and ideally at the nanoscale, allowing to access new and better properties in their applications.

F. Gschwind, O. Sereda, K. M. Fromm, *Inorg. Chem,***2009**, 48, 10535-10547.

F. Gschwind, K. M. Fromm, *Z. Anorg. Allg. Chem,***2011**, 1871-1879.

Investigating Mechanistic Pathways of Enzymatic Carbon-Sulfur Bond Formation

Carbon-sulfur bonds exist in a variety of bioactive molecules and are involved in detoxification processes and signal transduction. Many enzymatic pathways that form such C-S bonds, rely on metal-mediated activation of sulfur containing compounds. We have identified two enzyme types that share a similar active site and catalyze carbon-sulfur bond formation. Both enzymes activate their sulfur substrate by direct sulfur-metal ligation. However the reactions follow different chemical pathways. One enzyme type is iron dependent and catalyzes C-S bond formation, involving a 4-electron oxidation reaction, through a radical mechanism. The other enzyme can use various transition metals to activate its thioate substrate for nucleophilic attack on the electrophilic co-substrate. We are comparing the structural, kinetic and evolutionary data to understand the two different reaction types and the two different catalytic strategies.

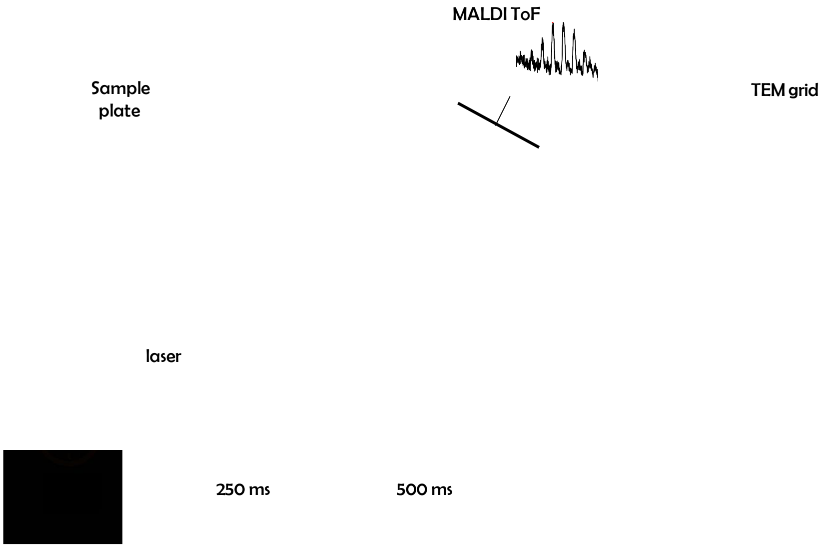
INTACT FLYING NANOPARTICLES FOR GAS-PHASE INVESTIGATIONS.

Almudena Gallego[1]*,Ugur Sezer[2], Markus Arndt[2] and Marcel Mayor[1].

[1] Chemistry Department, University of Basel, Switzerland.
[2]Faculty of Physics, VCQ, University of Vienna, Austria.

Sublimation of heavy particles as intact entities is a difficult challenge as large particles tend to decompose or fragmentize before the sublimation temperature is reached. However, it is a fundamental requirement when the physical behaviour of isolated entities in the gas-phase is to be investigated. Interferometry experiments of heavy particles are our ultimate goal[1]. Thus, we developed a system that allowed us to achieve the first key step of our research: the sublimation and characterization of intact nanoparticles (NPs). Although some evidences of sublimed NPs were already reported[2,3], its characterization as intact flying entities was not testified.

With this purpose, we synthesize metallic NPs stabilized with perfluorinated ligands in order to reduce the delocalized electron density on the carbon frames of the shell. It generates low-polarized particles and minimizes the particle-particle and particle-surface interactions. The NPs were vaporized with a laser desorption method and characterized with MALDI-ToF spectroscopy. The value of mass detected perfectly correlates with the one previously obtained under standard conditions and its resolution confirms that the ligands remain attached to the core of the NPs.



This experiment not only represents a key stage for the subsequent quantum experiments, but also shows the potential of combining chemical design with an accurate built-up technology, opening a range of new possibilities for energy and/or biological applications.

---

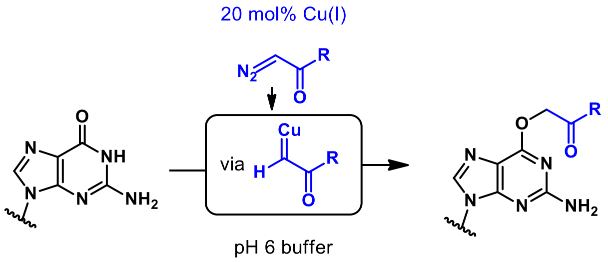
[1] Nat. Phys., 2014, 10, 271
[2] J. Opt. Soc. Am., 2014, 31, C15
[3] Nat. Nanotechnol., 2007, 2, 486

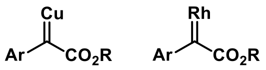
Electrophilic Cu(I) Carbenes Lead to Selective O^6G Alkylations

Stefanie Geigle, Dennis G. Gillingham

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

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.





prevoius work has shown that donor-acceptor substituted metal carbenes modify all exocyclic NH bonds in DNA and RNA (*i.e.* G, A, C)

Previous work from our group showed that nucleic acids can be catalytically modified with Rh(II) or Cu(I)-carbenes generated from α-diazocarbonyl compounds [1, 2]. The single stranded DNA and RNA motifs are alkylated selectively targeting the exocyclic N-H bonds of the nucleobases. However alkylation yields (especially for Cu(I)-carbenes) are moderate due to numerous N-H bonds in oligonucleotides. In contrast unstabilized Cu(I) carbene derived from ethyl α-diazoacetate is highly selective for O^6-alkylation when reacting with guanosine and inosine monophosphates, cleanly delivering a single product. Alkylation of other monophosphates was very slow delivering low levels of products. Investigation of larger nucleic acids verified the preference for O^6-alkylation. Switching to diazoacetamides showed the highest conversion so far, maintaining the O^6-selectivity, whereas the stable amide offers an opportunity to install further functionality.

[1] K. Tishinov, K. Schmidt, D. Häusinger, D. G. Gillingham, *Angew. Chem. Int. Ed.* **2012**, 51, 12000.

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

TiO_2 and Ag-doped TiO_2 nanocontainers as photocatalysts for CO_2 reduction

N. Hérault[1], K.M. Fromm[1]

[1]University of Fribourg, Department of Chemistry, Chemin du Musée 9, 1700 Fribourg

CO_2 gas is one of the major factors of the climate imbalance. Some solutions are proposed to convert CO_2 gas into more valuable molecules (such as CH_4, CH_3OH etc.). The reduction of CO_2 by photocatalysis pathway is interesting to scientists since the energy requirement of CO_2 reduction in the photocatalysis process is lower than in other processes and may be activated by solar light [1]. For this process, titanium dioxide-based materials with various structures are commonly used as photocatalysts [2], [3]. Moreover, TiO_2 can be doped with small metal islands (such as Pt, Ag, Au [1], [4]) used as electron traps to increase its efficiency (Fig. 1).

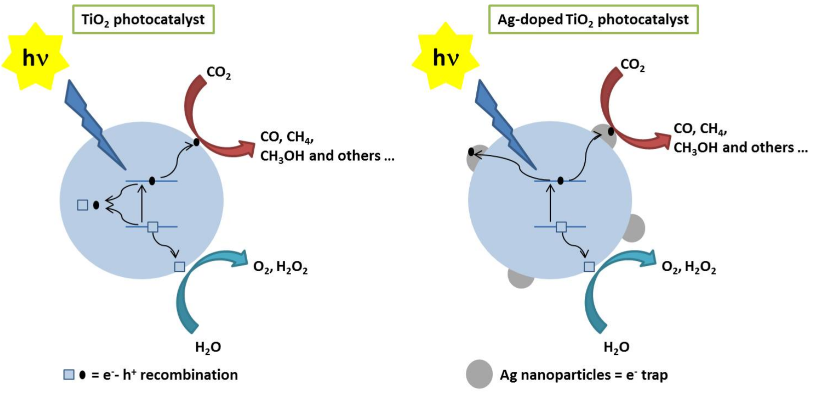


Fig.1. Schemes of basic mechanism of the TiO_2 and Ag-doped TiO_2 photocatalytic process

In this project, TiO_2 nanocontainers (NCs) were synthesized to evaluate the structural and the morphologic effects on their photocatalytic properties. Then TiO_2 NCs were doped with silver nanoparticles (NPs) to separate e^- h^+ pairs formed under light exposure and to enhance their lifetime. The synthesis principle is based on the TiO_2 coating on the surface of template beads containing Ag NP (illustration given in Fig. 2).

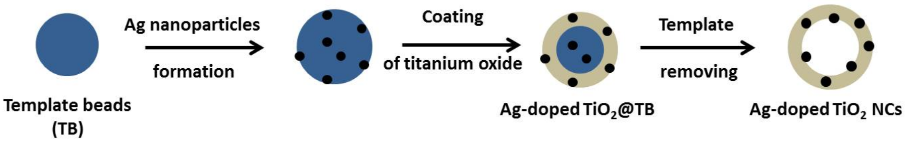


Fig. 2. Schematic illustration of the Ag-doped TiO_2 nanocontainers synthesis

[1] P. Usubharatana, D. McMartin, A. Veawab, P. Tontiwachwuthikul, *Ind. Eng. Chem. Res.* **2006**, 45, 2558-2568.

[2] T. Wanga, X. Menga, P. Lia, S. Ouyangb, K. Changa, G. Liua, Z. Meia, J. Ye, *Nano Energy*, **2014,** 9, 50–60.

[3] P-Q. Wang, Y. Bai, J-Y Liu, Z. Fan, Y-Q. Hu, *Catal. Commun.* **2012**, 29, 185–188.

[4] W-N. Wang, W-J. An, B. Ramalingam, S. Mukherjee, D.M. Niedzwiedzki, S.Gangopadhyay, P. Biswas, *J. Am. Chem. Soc.* **2012**, 134, 11276−11281.

Plenary Lecture, Poster

Hydrogels with short peptides and their composites with metal nanoparticles

A. Holzheu[1], K. Fromm[1]*

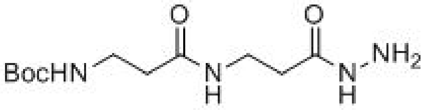
[1]University of Fribourg

A Hydrogel is a diluted polymer network with given structure and network properties obtained by either intermolecular - or by interfibrillar - crosslinks[1]. Both systems have certain advantages and disadvantages. Depending on the purpose one decides which system to use. In this case the project focuses on peptide self-assembled hydrogels which are formed by interfibrillar crosslinks. Peptide hydrogels are a promising class of soft biomaterials for cell culture, regenerative medicine, or drug delivery applications having advantages in biocompatibility, biodegradability and injectability[2,3].

In this case the hydrogel system (see figure) itself can synthesize silver nanoparticles due to its hydrazide end group. As it is already known for centuries that silver possesses antimicrobial properties, we propose a silver nanoparticle hydrogel system which can be used for medical purposes against multidrug-resistant bacteria[4,5].

Furthermore, the self-assembly process of dipeptide hydrogel systems like this one is still not 100 % understood. Scientists propose that the major driving force is π-π stacking. Other forces known to play a role are hydrophobic interactions, ionic interactions, hydrogen bonding and electrostatic interactions[6,7].

This project could help to further understand the self-assembly process as the dipeptide hydrogel system Boc(βala)$_2$N$_2$H$_3$ itself does not contain any aromatic groups. Therefore, π-π stacking cannot be the major driving force for self-assembly.
The aim is thus to synthesize the dipeptide hydrogel Boc(βala)$_2$N$_2$H$_3$ and to analyze its chemical, physical and mechanical characteristics with or without the incorporation of silver and to test its suitability for biological applications.



[1] A. Dasgupta et al., *RSC Advances*, **2013**, 3, 9117-9149
[2] S. Marchesan, L. Waddington, C.D. Easton, D.A. Winkler, L. Goodall, J. Forsythe, P.G. Hartley, *Nanoscale,* **2012,** 4*,* 6752-6760
[3] W.Y. Seow, C.A.E. Hanser, *Materials Today*, **2014**, 17, 381-388
[4] S. Eckhardt, P.S. Brunetto, J. Gagnon, M. Priebe, B. Giese, K. Fromm, *Chem. Rev.*, **2013**, 113 (7), 4708–4754
[5] M. Rai, A. Yadav, A. Gade, *Biotechnology Advances*, **2009**, 27, 76–83
[6] M. Tena-Solsona, S. Alonso-de Castro, J.F. Miravet, B. Escuder, *J. Mater. Chem. B*, **2014**, *2*, 6192-6197
[7] G. Fichmann, E. Gazit, *Acta Biomaterialia*, **2014**, 10, 1671-1682

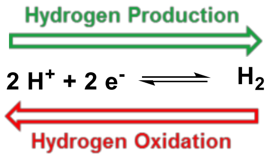
Hydrogenase Mimics using the Biotin-Streptavidin Technology

Sascha Keller, A. Dutta, P. Rodriguez, O. Rüdiger, O. Wenger, W. J. Shaw, T. R. Ward

University of Basel, Department of Chemistry, Spitalstrasse 51

Abstract

Storing energy from sustainable resources is one of the key challenges of current chemical research. One of the most efficient ways of achieving this, is to store electric energy into chemical bonds. In this context, the molecule of choice is dihydrogen. Indeed, the following reaction:



This reversible homolytic bond cleavage reaction is facilitated by transition metal catalysts. In this context, Ni-based hydrogen oxidation catalysts developed by Dr. Wendy Shaw ($Ni(P_2N_2)_2$ hereafter) display frequencies approaching those of natural hydrogenases (Fig. 1).[1,2] Despite their efficiencies, these homogeneous systems lack the second coordination sphere reminiscent of natural enzymes.

We speculate that introduction of such $Ni(P_2N_2)_2$-complexes within a protein environment may allow to fine-tune the second coordination sphere, to ultimately improve the efficiency of the resulting artificial hydrogenase. For this purpose, introduction of a biotin anchor on the ligand-scaffold (biot-P_2N_2) ensures that upon addition of streptavidin (Sav), the $Ni(P_2N_2)_2$ complex is quantitatively incorporated within streptavidin ($Ni(biot\text{-}P_2N_2)_2\cdot Sav$ hereafter).[3]

Preliminary studies demonstrate that $Ni(biot\text{-}P_2N_2)_2\cdot Sav$ affords an active hydrogenase. Although the activity of $Ni(biot\text{-}P_2N_2)\cdot Sav$ is significantly lower than that of the parent $Ni(P_2N_2)_2$ complex, site directed mutagenesis allows to fine tune the activity of the resulting hydrogenase.

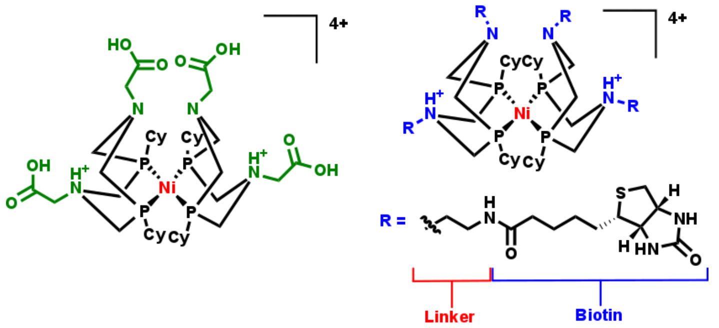


Fig 1: Introduction of a biotinylated nickel cofactor Ni(biot $P_2N_2)_2$ within streptavidin affords an artificial hydrogenase that can be optimized by site directed mutagenesis.

References

[1] J. C. Fontecilla Camps et al., *Chem Rev* **107**, 4273 4303 (2007).
[2] A. Dutta et al., *Angew Chem Int Ed* **53**, 6487 6491 (2014).
[3] V. Koehler et al., *Nature Chem* **5**, 93 99 (2013).

Title	Forname	Surname	University
Ms.	Sarah-Luise	Abram	University of Fribourg
Mr.	Benoît	Baichette	
Ms.	Linda Maria	Bannwart	University of Basel
Ms.	Lucinda	Batchelor	EPF Lausanne
Dr.	Gerald	Bauer	
Mr.	Felix	Bobbink	EPF Lausanne
Ms.	Ina	Bodoky	University of Basel
Mr.	Valentin	Chabert	University of Fribourg
Mr.	Antonin	Clemenceau	
Ms.	Paula	Corcosa	University of Fribourg
Dr.	Basile	Curchod	Invited Speaker
Mr.	Lorenzo	Delarue Bizzini	University of Basel
Ms.	Michela	Di Giannantonio	University of Fribourg
Ms.	Galina	Dulcevscaia	
Ms.	Céline	Dubosson	
Mr.	Pascal	Engi	University of Basel
Ms.	Alba	Finelli	University of Fribourg
Mr.	Cornel	Fink	EPF Lausanne
Mr.	Sebastian	Flueckiger	University of Basel
Ms.	Almudena	Gallego	University of Basel
Ms.	Stefanie	Geigle	University of Basel
Mr.	Cecot	Giacomo	EPF Lausanne
Ms.	Kristina	Goncharenko	University of Basel
Ms.	Simone	Grendelmeier	ETH Zurich
Mr.	Jonathan	Grolms	EPF Lausanne
Mr.	Manuel	Hellstern	University of Basel
Dr.	Nelly	Hérault	University of Fribourg
Ms.	Anja	Holzheu	University of Fribourg
Dr.	Cédric	Invernizzi	Invited Speaker
Mr.	Loïc	Jeanbourquin	EPF Lausanne
Mr.	Guojun	Ke	University of Basel

Title	Forname	Surname	University
Mr.	Sascha	Keller	University of Basel
Dr.	Gregor	Kiefer	EPF Lausanne
Mr.	Maximilian	Klein	Universtiy of Basel
Mr.	Emmanuel	Kottelat	University of Fribourg
Ms.	Sonja	Kracht	University of Fribourg
Ms.	Charlotte	Laupheimer	
Mr.	Ronald	Lee	EPF Lausanne
Ms.	Fiorella	Lucarini	University of Fribourg
Mr.	Nicolas	Luisier	EPF Lausanne
Mr.	Hendrik	Mallin	University of Basel
Ms.	Sabine	Malzkuhn	University of Basel
Mr.	Mathieu	Marmier	EPF Lausanne
Mr.	Mickael	Montandon-Clerc	EPF Lausanne
Mr.	Dennis	Mueller	University of Fribourg
Mr.	Frederik	Neuhaus	University of Fribourg
Title	Forname	Surname	University
Mr.	François	Noverraz	EPF Lausanne
Ms.	Andrea	Pannwitz	University of Basel
Dr.	Alessandro	Prescimone	University of Basel
Mr.	Fabian	Schwizer	University of Basel
Mr.	Evgeny	Smirnov	EPF Lausanne
Mr.	Cédric	Stress	Universtiy of Basel
Mr.	Augustin A. S.	Tchawou Wandji	ETH Zurich
Dr.	Justus	Tönnemann	
Dr.	Hristo	Varbanov	EPF Lausanne
Mr.	Dmitry	Vasilyev	EPF Lausanne
Ms.	Noémie	Voutier	University of Fribourg
Mr.	Jérémy	Vuilleumier	
Dr.	James	Walton	Invited Speaker
Prof.	Stefan	Willitsch	Invited Speaker
Mr.	Jingming	Zhao	Universtiy of Basel