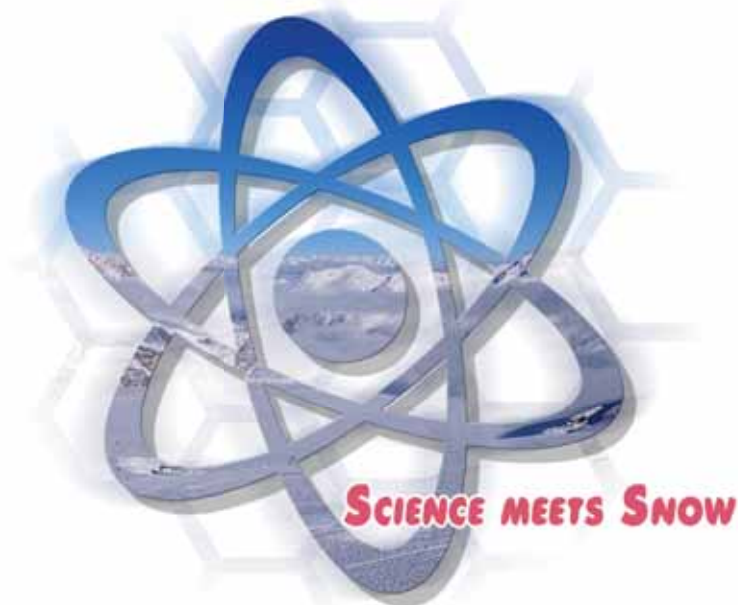




SCS
Swiss Chemical
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Chemists' Association



SwissSnowSymposium 2018

for young Scientists

Booklet of Abstracts

January 26-28, 2018

Hotel Alphubel

Saas Fee



Welcome to the SWISSNOWSYMPOSIUM 2018

Dear participants,

On behalf of the organizing committee, it is my pleasure to welcome you to the 16th SWISSNOWSYMPOSIUM in Saas-Fee.

We are delighted to announce that the 16th edition has fulfilled the high participation rate, derived from the success of previous editions, with more than 25 contributions divided in talks and poster sessions.

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

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

Along with the other members of the SYCA, I would like to extend a very warm welcome to the eight invited speakers: Prof. Peter Chen, Dr. Dmitry Perekalin, Mag. Matthias Rizzi, Dr. Sviatlana Siankevich, Dr. Matthew Wise, Dr. Justus Tönnemann, Delia Mihaila, and Dr. Gerald Bauer, as well as to our generous sponsors whose kind contributions enable this event to take place.

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

Best wishes,

Cornel Fink
President, SYCA

We gratefully thank our sponsors



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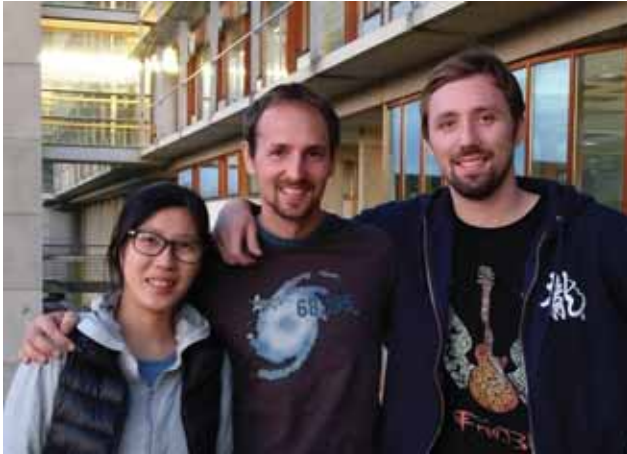
Ihr Schweizer Laborunternehmen. Seit 1986.

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Organizing Committee

Cornel Fink, President, SYCA
Dmitry Vasilyev, Vice President, SYCA
Lu Chen, Treasurer, SYCA



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 26, 2018

- from 17:00 Registration, Apéro
- 18:30 - 19:50 Dinner
- 20:00 - 20:05 Break
- 20:05 - 20:15 Words of Welcome: Cornel Fink, President SYCA and Chair of SSS'18
- 20:15 - 21:15 **Invited lecture: Prof. Peter Chen, Full Professor, ETH Zürich**
«Bond strengths in the gas phase, in solution, and in silico: dispersion effects and big molecules»
- 21:15 - 21:20 Break
- 21:20 - 22:00 **Invited lecture: Delia Mihaila, MDPI**
«The Impact of Open Access in Scholarly Publishing. The Role of MDPI in a Changing World»
- 22:00 - 22:05 Break
- Panel discussion: Perspectives with a PhD degree**
Dr. Sviatlana Siankevich, CTO & Co-founder, Embion Technologies SA
- 22:05 - 23:25 **Dr. Matthew Wise, Corporate Strategy, ABB**
Dr. Justus Tönnemann, Chemist Quality Assurance & Quality Systems, Carbogen Amcis
Dr. Gerald Bauer, Postdoctoral researcher, PSI
- 23:25 - 23:30 Break
- 23:30 - 00:10 **Session 1 (Chair: Cornel Fink)**
- 23:30 - 23:50 Lucinda Batchelor, EPFL
- 23:50 - 00:10 Giacomo Cecot, EPFL

Saturday, January 27, 2018

- 17:15 - 18:15 **Invited lecture: Dr. Dmitry S. Perekalin, Researcher, Russian Academy of Sciences**
«Cyclobutadiene complexes of platinum metals»
- 18:05 - 18:25 **Session 2 (Chair: Dmitry Vasilyev)**
- 18:05 - 18:25 Zhangjun Huang
- 18:30 - 19:45 Dinner
- 19:45 - 20:15 Poster session
- 20:15 - 20:20 Photo Session
- 20:20 - 21:20 **Invited lecture: Mag. Matthias Rizzi, Expert Process Safety, Consulting International**
«Quantitative ATEX-HAZOP - A holistic Approach tackling Process Safety by combining Risk and Ignition Source Analysis with Numerical Methods»
- 21:20 - 21:25 Break



21:25 - 00:00	Session 3 (Chair: Dmitry Vasilyev)
21:25 - 21:45	Aswin Gopakumar
21:45 - 22:05	Martin Sommer
22:05 - 22:25	Linda Bannwart
22:25 - 22:30	Break
22:30 - 22:50	Xinjiang Cui
22:50 - 23:10	Dmitry Vasilyev
23:10 - 23:30	Cornel Fink
23:30 - 23:45	Break
23:45	Awards

Sunday, January 28, 2018

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

SwissSnowSymposium 2018 - 26.-28.01.2018



Bond strengths in the gas phase, in solution, and in silico: dispersion effects and big molecules

Prof. Dr. Peter Chen

Laboratorium für Organische Chemie, ETH Zürich

Van der Waals attractive forces have often been neglected because each individual interaction is small. Nevertheless, for organic and organometallic molecules of distinctly moderate size, e.g. 100-200 atoms, the large number of small, attractive interactions lost upon cleavage of a covalent bond can add up to a significant contribution to the bond dissociation energy, in the range of tens of kcal/mol. Whereas structural evidence for an “extra” stabilization has been reported, experimental measurement of bond dissociation energies for large molecules in the gas phase are surprisingly rare. We report a comprehensive study of 36 proton-bound dimers for which a central $^+N-H\cdots N$ bond is constant, but the number and extent of non-bonding interactions can be varied systematically. We report experimental BDE measurements in the gas phase, and in solution, accompanied by computational studies using DFT and DLPNO-CCSD(T) methods taken to the CBS limit. Moreover, we include solvation with dispersion-corrected PCM models. We find that dispersion does indeed make a net attractive contribution to bond dissociation energies in the gas phase, amounting to tens of kcal/mol, but that this contribution is largely canceled out in solution, thus bringing the gas-phase observations of van der Waals attraction and the solution observations of steric repulsion into agreement. We present ideas on how this more detailed knowledge of an universal, non-covalent interaction may be manipulated rationally to modulate bond strengths, in general.

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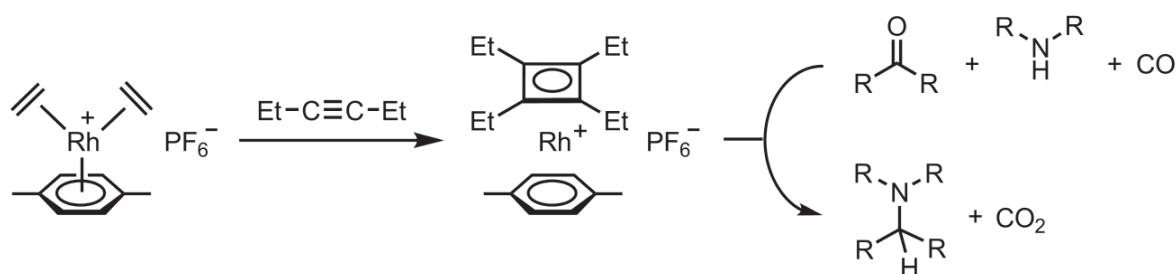
Cyclobutadiene complexes of platinum metals

Dmitry S. Perekalin

Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences

Complexes of platinum metals are widely used as catalysts in modern organic chemistry. They are usually equipped with phosphine, carbene or cyclopentadienyl ligands, which help to stabilize the active metal center and to control the selectivity of reactions. At the same time, surprisingly, complexes with cyclobutadiene ligands have not been used in catalysis prior to 2015. Apparently, their application is hampered by their more complicated synthesis, which stems from instability of the cyclobutadiene as a free ligand. The most common method for synthesis of the cyclobutadiene complexes is the dimerization of alkynes in the coordination sphere of a metal. However, this approach suffers from the inherently high reactivity of alkynes, which often leads to formation of oligomerization products [1].

Recently, we have developed a new general method for the synthesis of the cyclobutadiene rhodium complexes [2]. The key idea was to use a metal precursor with only two coordination sites for incoming alkynes in order to suppress the unwanted oligomerization. Indeed, the substitution of two labile ethylene ligands in the rhodium complex $[(C_2H_4)_2Rh(p\text{-xylene})]PF_6$ by 3-hexyne cleanly gave the desired cyclobutadiene complex $[(C_4Et_4)Rh(p\text{-xylene})]PF_6$. This compound provides an access to variety of other rhodium complexes and moreover appeared to be the most active catalyst for reductive amination of aldehydes and ketones in the presence of CO as deoxygenative agent.



This work was supported by the Russian Science Foundation (grant #17-73-20144).

[1] N. V. Shvydkiy, D. S. Perekalin, *Coord. Chem. Rev.* **2017**, *349*, 156–168.

[2] D. S. Perekalin, N. V. Shvydkiy, Y. V. Nelyubina, A. R. Kudinov, *Chem. Eur. J.* **2015**, *21*, 16344–16348.

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Quantitative ATEX-HAZOP - A holistic Approach tackling Process Safety by combining Risk and Ignition Source Analysis with Numerical Methods

Mag. Matthias Rizzi

TÜV SÜD Schweiz AG

The Hazard And Operability (HAZOP) Study is a powerful tool and as such widely used in Process Industry to assess risks, identify their root cause and describe their consequences. Specific risks, which are not primarily related to the process but to more general circumstances e.g. ATEX or Machine Safety, are often covered separately and not integrated properly into risk analysis. Moreover, these methods are of qualitative nature, which makes it difficult to implement them into a quantitative HAZOP study.

In the present work a holistic approach was developed to assess the risk from ionizing radiation as an ignition source in a quantitative manner. Numerical methods used in dosimetry were applied in order to identify potential root causes for igniting an explosive atmosphere. The results were implemented in an ignition source analysis according to ATEX standards and finally integrated into a quantitative HAZOP study.

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Saas-Fee, 26.-28.01.2018

Bridging the Gap: Crosslinking Allosteric Sites on the NCP

L. K. Batchelor¹, G. Palermo¹, T. Von Erlach¹, Z. Adhireksan², L. De Falco Jr², U. Röthlisberger¹, C. A. Davey², P. J. Dyson¹

¹EPF Lausanne, ²Nanyang Technological University (Singapore)

Dinuclear metal complexes have emerged as a promising class of biologically active molecules that display interesting anti-cancer activity and properties. As a consequence, both homo- and hetero-bimetallic combinations are being explored. An allosteric relationship between RAPTA-T, a ruthenium(II) anti-tumoral, and Auranofin, a gold(I) anti-rheumatic drug, is observed on nucleosome core particle (NCP). The binding of RAPTA-T to the surface of H2A-H2B dimer induces a kink in the long α -helix of the H2A histone protein that enables Auranofin to bind to two previously inaccessible sites.^{[1],[2]}

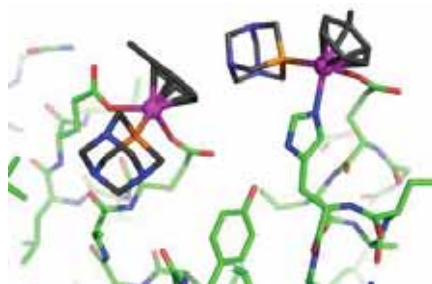


Figure 1. Binding sites of the RAPTA-T moiety on the histone component of the NCP.

This allosteric effect has been exploited to design and synthesize two generations of hetero-ruthenium(II)-gold(I) complexes. The design is based on crystallographic and computational data with the aim of simultaneously binding to the sites of the parent drugs, Auranofin and RAPTA-T, on the NCP. Here, we demonstrate that a single hetero-bimetallic ruthenium(II)-gold(I) complex can initiate the same allosteric effect as caused by the binding of mono-nuclear RAPTA-T and interact with the corresponding Auranofin site.

- (1) Z. Adhireksan, G. E. Davey, P. Campomanes, M. Groessl, C. M. Clavel, H. Yu, A. A. Nazarov, C. H. F. Yeo, W. H. Ang, P. Dröge, U. Rothlisberger, P. J. Dyson, C. A. Davey, *Nature Commun.* 2014, **5**, 3462.
- (2) Z. Adhireksan, G. Palermo, T. Riedel, Z. Ma, R. Muhammad, U. Rothlisberger, P. J. Dyson, C. A. Davey, *Nature Commun.* 2017, **8**.

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Production of Methanol from CO₂: Indirect approaches via N-formylation of aminesAswin Gopakumar, Paul Dyson

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CO₂ is an abundant, renewable, cost-effective and a green C1 source [1-4]. Owing to the relatively stable nature of CO₂, it is difficult to convert it into useful products like Methanol. Herein, we present our latest results on the indirect formation of Methanol via N-formylation of amines followed by hydrogenation. Heterogeneous catalysts based on metals and their oxides were employed for the reaction. Altogether, the procedure offers an efficient, green, viable, recyclable, reusable and a cost-effective approach to convert CO₂ into a fuel.

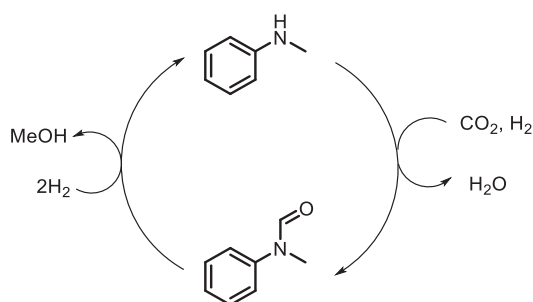


Fig 1. General scheme showing the formation of methanol from CO₂ via N-formylation of amines

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Polar ordering of macromolecular chains in biomimetic composite materials and natural tissues

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The state of alignment of macromolecules in biomimetic materials and natural tissues will be discussed by investigating a mechanism of electrical polarity formation: An in vitro grown biomimetic fluorapatite (FAp)/ gelatin composite is analyzed for its polar properties by second harmonic (SHGM) and scanning pyroelectric microscopy (SPEM). Growth media containing biological macromolecules do not only influence the morphology, but can also have a significant impact on the polarity of a composite [1]. Hexagonal prismatic seed crystals of FAp formed in gelatin represent a monodomain polar state due to aligned mineralized gelatin molecules [1]. Later growth stages, expressing a dumbbell morphology, develop into a bipolar state because of surface recognition by gelatin functionality.

Other inorganic materials like CaCO_3 (calcite), CaSO_4 and CaC_2O_4 formed analogous composites when grown in a gelatin matrix. In addition, all of these composites revealed a similar behavior regarding polarity formation as compared to FAp. Subsequently the gelatin matrix was replaced by other gels, such as agar-agar and carrageenan, which developed the same kind of bipolar state. By growing the inorganic components in tetramethylorthosilicate (TMOS, nonpolar gel), SPEM experiments did not reveal any polarity. In all grown composites, the only present organic and polar material are the polar gel macromolecules. Single crystals of the investigated inorganic components, e.g. FAp and CaCO_3 , are centrosymmetric. Therefore, the only possible origin of polarity in these biomimetic composites is due to the incorporated macromolecules.

Comparing SPEM data of natural hard tissues (teeth and bone) with biomimetic FAp/ gelatin, calcite/ gelatin and other investigated composites, a surprising analogy in view of growth-induced states of polarity is found: The development of polarity in vivo and in vitro can be explained by a Markov-type mechanism of molecular recognition during the attachment of macromolecules. Furthermore, SHGM was able to reveal the polar structure of tissues by the application of phase sensitive experiments and the use of a polar reference crystal [2].

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Synthesis of a Diacetylene Bridged Geländer-Type Oligomer

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Atropisomers are chiral compounds that do not contain stereogenic 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.¹ The interest in atropisomers started with the discovery that the configuration around a biphenyl axis is an important factor in controlling 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.² A new class of atropisomers was introduced in 1998 by Fritz Vögtle: the Geländer-Oligomers.³ In the classical Geländer oligomers the optically inactive meso form is more stable than its enantiomers. Recently, our group reported a novel type of Geländer oligomers that cannot exist as a meso form, but still undergo fast racemization.⁴⁻⁶ To enhance the stability of our new Geländer oligomers, we designed a series of more rigidly bridged biphenyls. Consequently, the racemization process in these atropisomeric molecules should be significantly slower. The poster will present the synthesis and further studies on diacetylene bridged Geländer oligomer **1**.

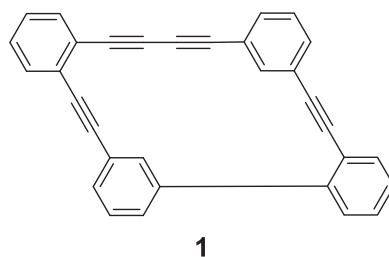


Figure 1: Diacetylene bridged Geländer oligomer **1**.

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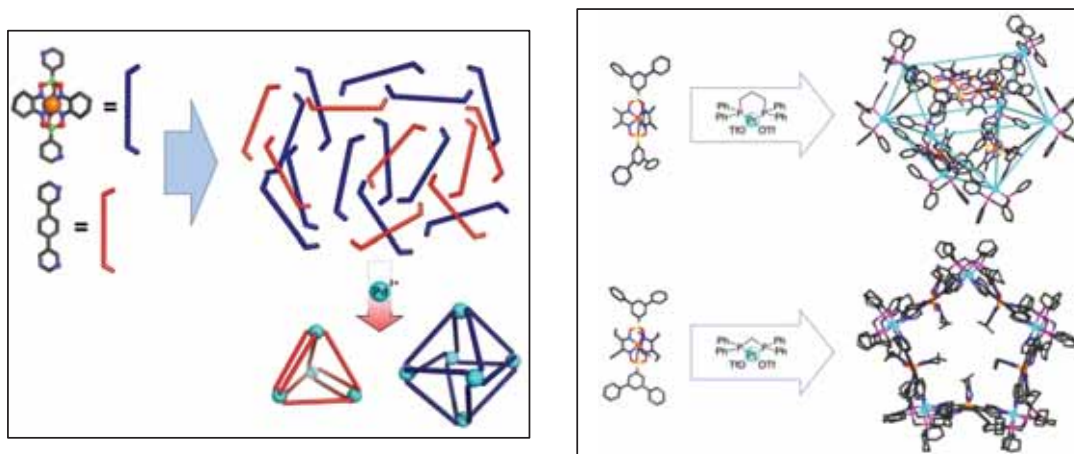
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The Importance of Subtle Steric Effects on Self-assembled Coordination Cages

Giacomo Cecot, Kay Severin

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The chemistry of coordination cages has advanced dramatically in recent years. Different synthetic approaches have been developed, allowing the efficient preparation of cages with diverse geometries and functions. The understanding of the influence of subtle steric effects is a central point in the rational design of supramolecular assemblies. Clathrochelate-based metalloligands enable the exploration of the yet not fully understood role of the aspect-ratio of building blocks towards the formation of different assemblies. Moreover, the utilization of metalloligands instead of simple organic polypyridyl ligands resulted in the formation of uncommon structures. With 'naked' Pd²⁺ ions, we observed octahedral complexes instead of tetrahedral ones.¹ With *cis*-blocked Pt^{II} complexes and tetratopic metalloligands, we obtained cages with unusual geometries and we started to explore the intricate structural chemistry of M^{II}_{2n}L_n-type assemblies.^{2,3} Overall, our results provide further evidence that rather small structural modifications can have an important effect on multicomponent self-assembly reaction. The anticipation and, ultimately, the control of such effects will enable chemists to construct synthetic assemblies of unprecedented complexity and functionality.



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Understanding the role of carbohydrate ligands in the immune response

Rachel Hevey¹, Manjula Nagala², Paul Crocker², Beat Ernst¹

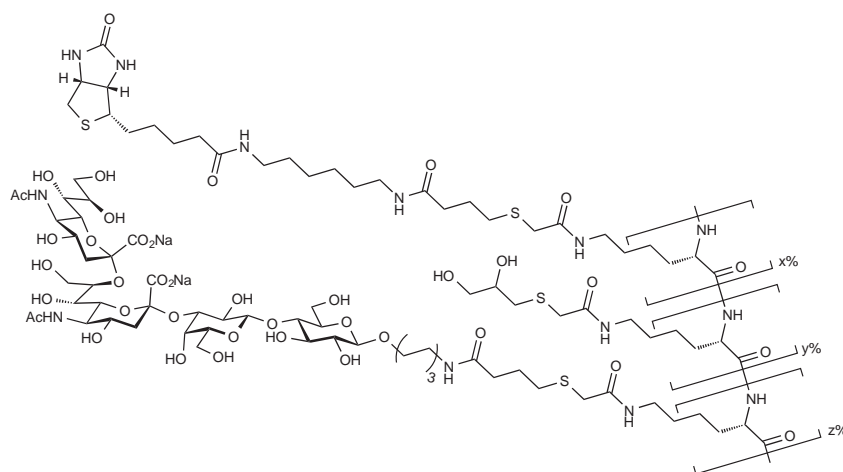
¹ Molecular Pharmacy, University of Basel

² School of Life Sciences, University of Dundee, UK

Carbohydrates are ubiquitous among all organisms, found intracellularly, extracellularly, and membrane-bound. They coat all cell surfaces and typically act as a first point of contact in cell communication, with carbohydrate-protein interactions inducing downstream biological effects.

Carbohydrate-protein binding events can both intensify (e.g. mannose-binding lectins) or suppress (e.g. siglecs) host immune responses. They are involved in normal cell-cell interactions necessary for maintaining homeostasis, such as membrane-bound carbohydrates used for the identification of 'self' cells, which inhibit immune cell activation. Alternatively, the aberrant expression of carbohydrates can facilitate disease, such as cancer cells and pathogens which both express mimics of 'self' carbohydrates to camouflage themselves, thereby repressing immune responses and enhancing their survival.

Owing to significant structural complexity, obtaining most oligosaccharides from natural sources has proven a major challenge, which in turn has limited their biological assessment. We have instead used chemical synthesis to obtain target molecules in sufficient scale and purity, and subsequently screened multivalent ligand displays against a siglec panel to gain information on ligand preference. High affinity interactions are currently being examined further in immune cell assays.



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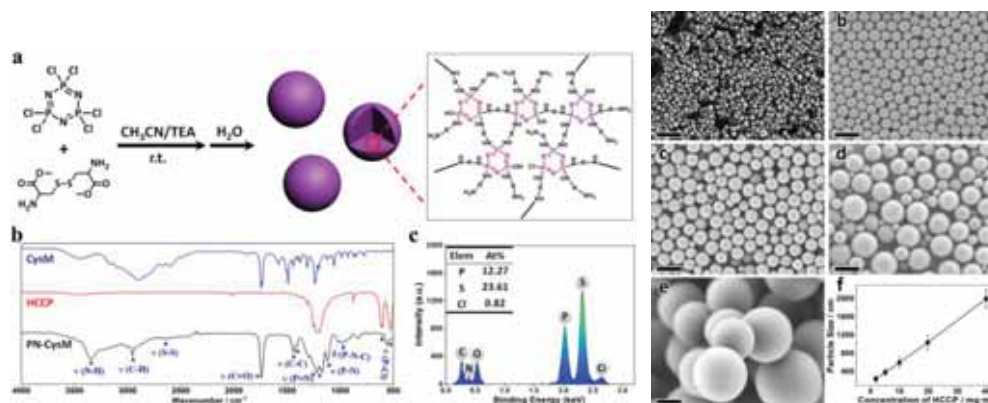
The Synthesis and Application of Cyclo-matrix Polyphosphazene Nanomaterials

Zhangjun Huang, Zhaofu Fei, Qinghua Lu, Paul Joseph Dyson

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Cyclomatrix-polyphosphazenes (C-PPZs) are a new class of nanomaterials that have attracted significant interest owing to their unique inorganic–organic hybrid structure and designable properties, which consist of an inorganic main chain (–P=N–) with two of the same or different organic side chains attached to each phosphorus atom. The C-PPZs exhibit versatile nano-morphologies and characteristics depending on the templates and substituents used. C-PPZs can be obtained easily and in large quantities by precipitation polycondensation or water triggered polycondensation reaction under ambient conditions. Phosphazene rings in the polymers are linked via exocyclic groups with organic monomers to form a highly crosslinked polymeric network. We firstly synthesized C-PPZs from biodegradable amino acid esters, the C-PPZs present size-adjustable uniform spherical nano-structure,^[1] and revealed that the morphologies of the C-PPZs depends on the solubility parameters of the C-PPZ oligomer solutions.^[2] We applied the biodegradable C-PPZ nanoparticles for drug delivery vehicles, applied porous C-PPZ nanoparticles for ionic liquids combined nanoreactors for CO₂ conversion, C-PPZ nanoparticle coatings on a honeycomb surface as hierarchical structures for bioapplication,^[3] and so on.



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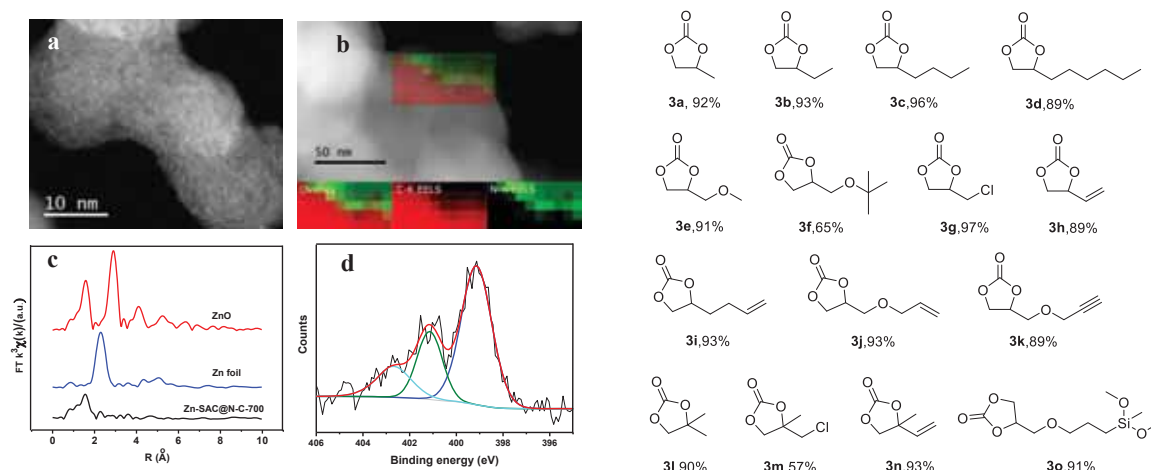
The effect of N species on the preparation of Zn-based single atom catalyst

Xinjiang Cui

ISIC, École Polytechnique Fédérale de Lausanne (EPFL), 1015 Lausanne, Switzerland.

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Recently, single atom catalysts (SAC's) provide new opportunities to design catalytic materials at the molecular level because the individual active metal centers can be controlled precisely by the nature of the neighboring atomic species[1]. Hence, we thought that such SAC's allow for improved catalytic activity due to metal utilization of up to 100%. Encouraged by recent investigations on the preparation and utilization of *N*-doped metal nanoparticles and single atom catalysts[2], here we describe the preparation, characterization and catalytic testing of a novel Zn single atom catalyst (Zn-SAC) supported on *N*-doped carbon material. The resulting catalyst allows for efficient and general activation of functionalized terminal epoxides to give the corresponding carbonates in high yields.



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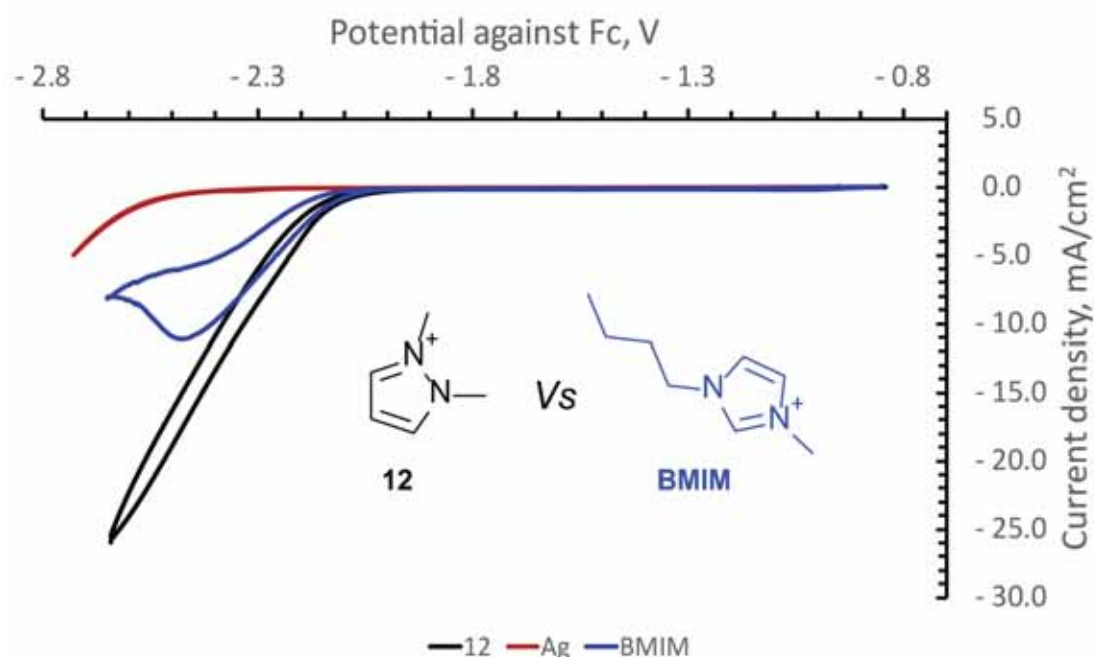
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Saas-Fee, 26.-28.01.2018

Pyrazolium ionic liquids for electrochemical reduction of CO₂

Dmitry Vasilyev, Paul Dyson
EPFL

Carbon dioxide electrochemical reduction is a promising approach to CO₂ valorization, but significant reduction overpotential hampers development of this method. Ionic liquids (ILs) were found to significantly reduce the overpotential [1], but the number of active co-catalysts is limited to very few classes of ILs (e.g. imidazolium [1] and pyrrolidinium [2] ILs). In this project series of pyrazolium liquids was synthesized and employed for electrochemical reduction of carbon dioxide. These co-catalysts showed enhanced performance compared with conventional imidazolium ILs. GC measurements confirmed good faradaic efficiencies and selectivity for carbon monoxide. It was shown, that the co-catalysts are getting more stable with increase of methyl ring substituents, and that additives of water significantly enhance the catalysis. Overall, pyrazolium ILs appear to be promising co-catalysts for CO₂ activation.



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The role of Formic Acid And Methanol in the hydrogen society

Cornel Fink, Gábor Laurenczy

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In face of global warming and rapid climate change, the world is looking for alternative ways to satisfy our constantly growing demand for energy. Harvesting power from renewable energy sources is seen as one of the most promising solutions. The fluctuating nature and seasonal changes of the underlying phenomena require means of storage. The formic acid hydrogen storage cycle offers properties which makes it suitable system for hydrogen storage and delivery on demand.^[1,2] The homogeneous catalytic reduction of carbon dioxide with hydrogen yields in a first reduction step formic acid (53 g/L H₂). Under the suitable conditions, the reaction continues to methanol, storing two equivalents of hydrogen, which makes the compound a more favorable fuel for mobile application since the gravimetric energy density is higher (99 g/L H₂).^[3]

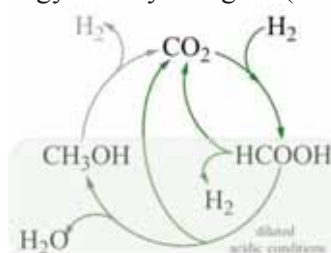


Figure 1 The carbon dioxide – formic acid – methanol cycle for hydrogen storage and delivery.

Homogeneous catalysts for FA dehydrogenation are well-studied and exist in great number.^[4] It is well known that the dehydrogenation of formic acid is an endothermic process. Driven by the entropic term, including the liberation of two mole equivalents of gas, the reaction occurs by absorbing energy from its environment. Pressurized reaction calorimetry is a well-suited tool to follow this process and even more to quantify the heat flow necessary to dehydrogenate a defined quantity of formic acid. Based on this measurements, thermodynamic data for catalytic formic acid dehydrogenation under realistic conditions is obtained, which are important tools for planning formic acid storage devices.

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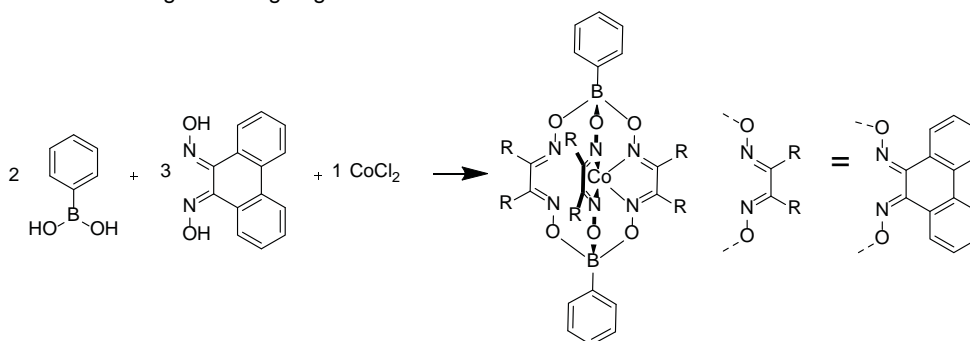
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Clathrochelates as redox-active building blocks

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Clathrochelates are metalloligands which can be easily accessed using a one-pot procedure.¹ Our research group recently reported the assembly of novel supramolecular cages using these metalloligands as building blocks.² In this report, we present Fe^{II} and Co^{II} clathrochelates as redox-active building blocks made from a variety of non-innocent dioximes. Cyclic voltammetry experiments were performed on each building block. As Fe^{II} clathrochelates tend to have lower reduction potential than Co^{II} clathrochelates, mixing these Co^{II} ligands with transition metals allow for the formation of new redox-active supramolecular assemblies such as coordination cages. Cyclic voltammetry studies on the Co^{II} associated coordination cage are on going.



Scheme 1. Synthesis of Co^{II} phenyl-phenanthrenato clathrochelate

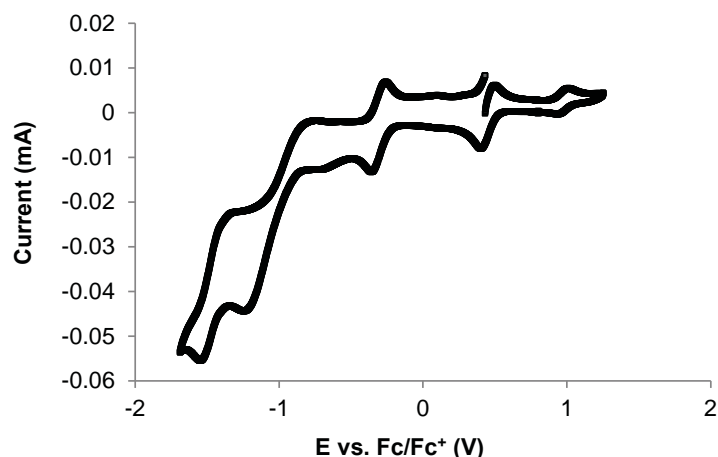


Figure 1. Cyclic voltammogram of Co^{II} phenyl-phenanthrenato clathrochelate in CH₂Cl₂, (0.1 M nBu₄NPF₆, 150 mVs⁻¹, platinum counter electrode).

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Elucidating the structure-activity relationship of minigastrin with the cholecystokinin receptor subtype 2

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Radiolabelled minigastrin derivatives are used to target the cholecystokinin receptor subtype 2 (CCK2R) which is overexpressed on neuroendocrine tumors.^[1] The pentaglutamic acid sequence of minigastrin plays an important role regarding receptor binding and kidney uptake, but the interactions and structural influences on a molecular level are not fully understood. We investigated the structure activity relationship of minigastrin with the CCK2R by replacing the pentaglutamic acid sequence in minigastrin with linkers differing in their flexibility and the number of anionic charges. The structural variations include a flexible aliphatic linker, a linker with only three D-Glu residues and a structured linker with four adjacent β^3 -glutamic acid residues. PP-F11N (DOTA-[D-Glu¹⁻⁶, Nle¹¹]gastrin-13) was used as the lead compound for comparison. Conjugation to 1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetic acid (DOTA) allowed radiolabelling of the peptide derivatives with ¹⁷⁷Lutetium. The *in vitro* properties (IC₅₀, internalization and serum stability) and the *in vivo* behavior in tumor bearing mice were evaluated with a human medullary thyroid cancer cell line (MZ-CRC1). Molecular modelling was used for the identification of specific interactions between our ligands and residues within the binding site of a CCK2R homology model.



IC₅₀ values were obtained in the low nanomolar range (15-35 nM), with the aliphatic elongated peptide as the only exception with almost one order of magnitude higher values (>100 nM). *In vitro* internalization into MZ-CRC1 cells was in line with the observed *in vivo* tumor uptake. The tumor uptake was dependent on the amount of anionic charges and structural features present and increased in the following order: no linker \leq aliphatic sequence < (D-Glu)₃ sequence < (β^3 -Glu)₄ sequence < (D-Glu)₆ sequence. The observed experimental data can be explained by our modelled ligand-CCK2 homology receptor model complex. A better understanding of the molecular structural binding behaviour of peptidic CCK2R ligands enables an improved rational design of such ligands.

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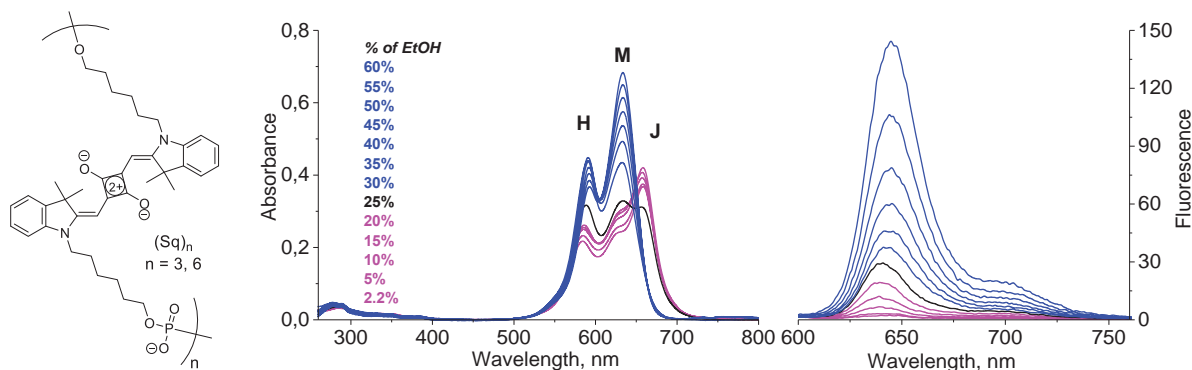
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Aggregation properties of phosphodiester-linked squaraine oligomers in aqueous solutionsLarysa Markova, Robert Häner

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In the search for new compounds for supramolecular chemistry we synthesized the squaraine oligomers (Sq_3) and (Sq_6), and studied their spectral properties in aqueous solutions. The synthesis of the oligomers was performed by a phosphoramidite approach. Absorption and fluorescence spectra of the oligomers were measured in aqueous solutions containing various concentrations of ethanol.



Absorption (left) and fluorescence (right, $\lambda_{ex} = 585$ nm) spectra of the oligomer (Sq_3) depending on the concentration of ethanol in the aqueous solution. Conditions: 1 μ M of the oligomer, 10 mM phosphate buffer, 100 mM NaCl

Absorption spectra and fluorescence intensities strongly depend on the ethanol content. At concentrations below 20%, the absorption spectrum of (Sq_3) shows the splitting of the main band (632 nm) into a long-wavelength shifted J-band (658 nm) and a short-wavelength shifted H-band (585 nm), which corresponds to an oblique orientation of the transition dipole moments. Ethanol contents above 30% reveal only absorption due to monomer and H-aggregate. The degree of H-aggregation decreases with increasing quantity of ethanol. The absorption spectrum of oligomer (Sq_6) demonstrates a similar response to the change of ethanol percentage. Fluorescence of the oligomers (Sq_3) and (Sq_6) is nearly undetectable at minimal ethanol concentration (2%). Upon increasing the ethanol concentration, the fluorescence intensity grows, which is explained by dissolution of non-emissive aggregates.

Due to their ability to form supramolecular aggregates in aqueous solutions and their absorption properties in the long-wavelength region of the visible spectrum, the amphiphilic squaraine oligomers shown here are promising compounds as components of new materials with diagnostic, biomedical and electronic applications.

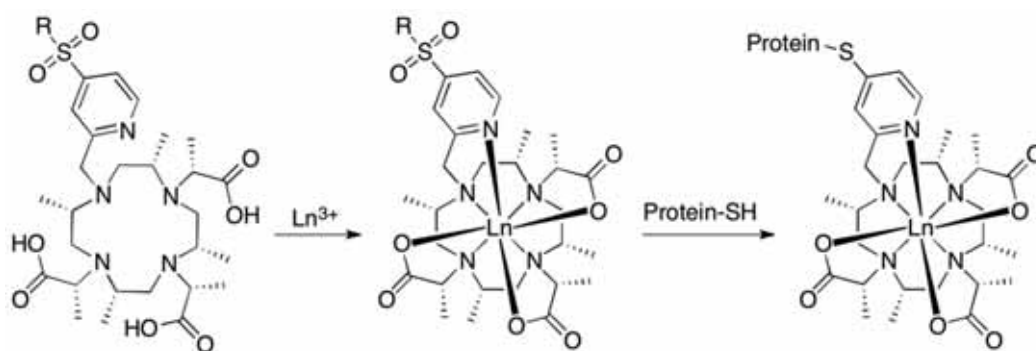
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Improved lanthanide chelating tags for *in vitro* and *in cellulo* pseudo-contact shift NMR spectroscopy.Thomas Müntener¹, Daniel Häussinger¹¹Department of Chemistry, University of Basel, St. Johannis-Ring 19, 4056 Basel, Switzerland

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Pseudocontact shift (PCS) NMR spectroscopy is a powerful tool to study the structures and interactions of proteins and other biomacromolecules in solution.^[1] High affinity chelating tags displaying a rigid conformation around the lanthanide metal centre are particularly well suited for creating large PCSs. We have used a seven-fold methylated DOTA scaffold and a pyridine-sulfone linker to create a lanthanide chelating tag (LCT) that fulfils the above criteria and that is, in addition, stable towards strongly reducing buffer conditions as they are found e.g. in living cells.^[2] Figure 1 depicts the reaction scheme for the loading of the tag with lanthanide cations and the conjugation to a surface exposed cysteine of a protein to form a thioether bond. Thioether bonds are very inert not only to strongly reducing potentials, but also towards nucleophilic substitution in aqueous solution as well as extreme pH conditions. The new family of LCTs allows therefore to monitor long-range interactions > 60Å under conditions that were not accessible previously and thus bear a great potential to study proteins and their interactions in virtually any buffer composition.

**Figure 1.** Reaction scheme for the metallation and conjugation of the new tags.

Here we wish to present preliminary data on a further modified LCT leading to improved properties for PCS NMR spectroscopy. The fluorine substituted analogue of DOTA-M7Py shows an enhanced reactivity towards selective cysteine labelling under neutral conditions at 20-25°C. The tags deliver large PCS > 6 ppm and cause strong alignment of the tagged protein with the magnetic field and give thus rise to ample residual dipolar couplings > 30 Hz.

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Plug-and-play multicolor fluorogenic sensors for imaging analytes in real time

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Optical biosensors play an essential role in our current understanding of the function of intracellular analytes in cell signaling. Herein, we describe the first protein-based fluorogenic biosensor in which the recognition of an intracellular analyte conditions reversibly the binding and activation of an exogenously applied fluorogenic ligand. Our sensor uses genetically encoded Fluorescence-Activating and absorption-Shifting Tag (FAST) variants, which bind and activate the fluorescence of synthetic fluorogens, conformationally coupled to analyte recognition modules so that analyte binding enhances fluorogen binding and thus fluorescence. This promising approach allowed us to generate multicolor plug-and-play fluorogenic biosensors for imaging the intracellular levels of Ca^{2+} in living mammalian cells in real-time.

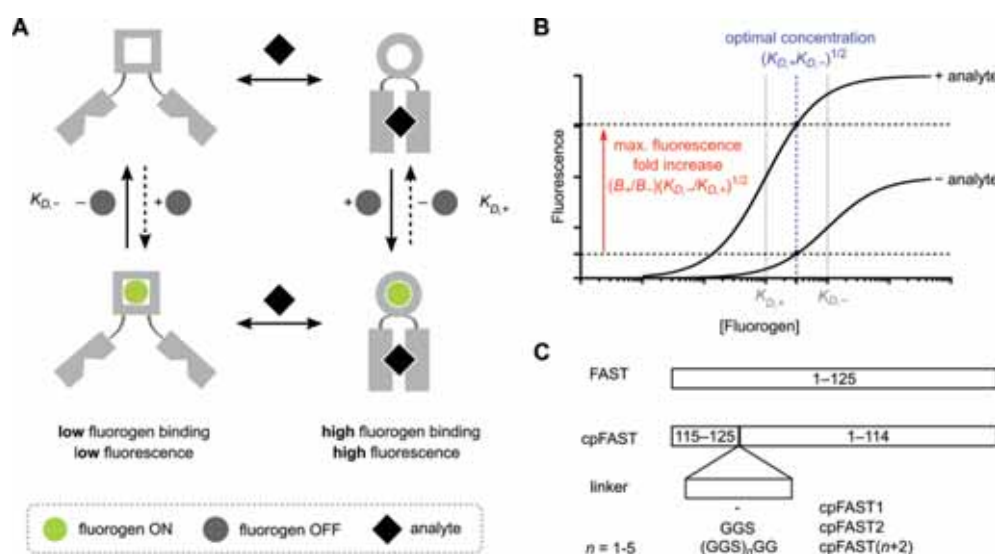


Figure. Development of FAST-based optical biosensors. (A) Fluorogenic biosensors composed of a FAST variant coupled to analyte-recognition modules in which the binding of the fluorogenic ligand, and thus the fluorescence, is conditioned to the binding of the analyte. $K_{D,-}$ and $K_{D,+}$ are the thermodynamic dissociation constants of the sensor:fluorogen complex in the absence and the presence of analyte, respectively. (B) Simulated fluorogen binding curves in the presence and absence of analyte (with $K_{D,-} = 10K_{D,+}$). B_{-} and B_{+} are the brightness of the sensor:fluorogen complex in absence and presence of the analyte, respectively. (C) Circular permutations of FAST generated in this study.

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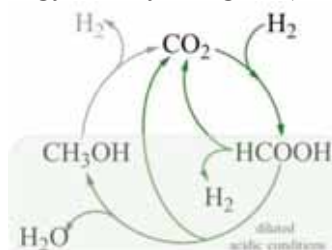


Figure 1 The carbon dioxide – formic acid – methanol cycle for hydrogen storage and delivery.

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