CHIMIA

CHIMIA 2019, Volume 73
ISSN 0009-4293
www. chimia.ch
Supplementa to Issue 7-8/2019

SCS
Swiss Chemical
Society

SCS Fall Meeting 2019
Poster Abstracts

# Session of Inorganic & Coordination Chemistry

September 6, 2019
Irchel Campus, University of Zürich, Switzerland
http://scg.ch/fallmeeting/2019

Swiss Chemical Society
Haus der Akademien
Postfach
3001 Bern
Switzerland
info@scg.ch
www.scg.ch

# Ligand Tuned Multinuclear Copper Complexes as Homogenous Water Oxidation Catalysts

D. Adiyeri Saseendran[1], G. R. Patzke[1]*

[1]Department of Chemistry, University of Zurich, Winterthurerstrasse 190, CH-8057 Zurich, Switzerland

Over the past few decades, the emerging understanding of nature's cubane {$CaMn_4O_5$} oxygen evolution complex has inspired the scientific world to develop homogeneous catalysts for artificial photosynthesis thereby converting solar energy to chemical fuels.[1] Although a sustainable approach, artificial photosynthesis is both kinetically and thermodynamically challenging, which increases the need for superior catalysts. Since then, many transition metal-based homogeneous catalysts have been developed in target to mimic the activity of the oxygen evolution complex.[2] However, stability issues such as metal leaching and ligand degradation/oxidation cause the catalysts to decrease their activity over time. Hence, the selection of appropriate metal and ligand is of utmost importance. Copper, an earth abundant and less toxic metal is often accounted for its unique redox properties. Since the appearance of the first homogeneous copper-bipyridine electrocatalyst for water oxidation[3], the use of copper metal for further investigations in homogeneous water oxidation is expected to be promising. Along with copper, a ligand with greater stability under harsh oxidation conditions and much donor capacity is selected. Recently, the 2-(2'-pyridyl)-2-propanoate (Pyalk) / 2-(2'-pyridyl)-2-propanol (PyalkH) ligand has been identified to stabilize high oxidation states of metal centers without undergoing self-degradation under extreme oxidative conditions.[4] Previous reports on water oxidation activity of copper molecular catalysts was identified to have major dependence on the ligand environment and nuclearity of the metal core, thus making it available for both photo and electrocatalytic water oxidation. Given the above, the objective of our work was focused on investigations for water oxidation activity of catalysts by ligand tuning using suitable precursors.

Along the lines of the above approach, two binuclear copper complexes were synthesized, namely: $Cu_2(pyalk)_2(OAc)_2(H_2O)_2$ and $Cu_2(pyalk)_2(pyalkH)_2(ClO_4)$. The catalysts were structurally characterized by single crystal X-ray diffraction, powder X-ray diffraction, and high-resolution ESI mass spectrometry. The electronic and optical characterizations were carried out with UV-Vis and FT-IR spectroscopy in solutions. Furthermore, the catalysts were screened for water oxidation activity under both photochemical and electrochemical conditions in order their performance to be compared. The photocatalytic oxygen evolution under different pH conditions was monitored by gas chromatography and Clark electrode kinetics.

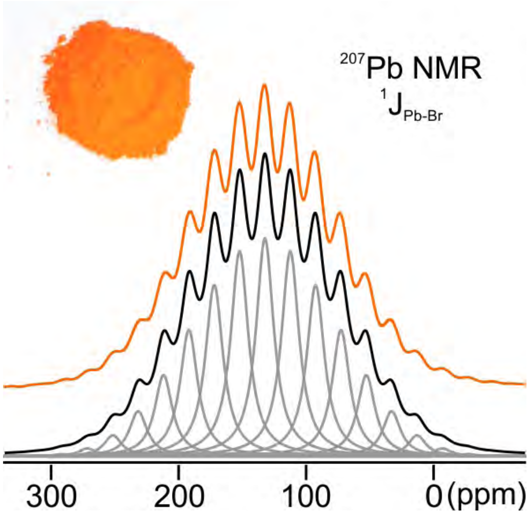
[1] X. Jiang, J. Li, B. Yang, X. Z. Wei, B. W. Dong, Y. Kao, M. Y. Huang, C. H. Tung, L. Z. Wu, *Angew. Chem.* **2018**, *57*, 7850–7854.
[2] M. Yagi, M. Kaneko, *Chem. Rev.* **2001**, *101*, 21–35.
[3] S. M. Barnett, K. I. Goldberg, J. M. Mayer, *Nat. Chem.* **2012**, *4*, 498–502.
[4] R. H. Crabtree, K. J. Fisher, H. M. C. Lant, T. K. Michaelos, G. W. Brudvig, L. S. Sharninghausen, D. Y. Shopov, S. B. Sinha, *Acc. Chem. Res.* **2017**, *50*, 952–959.

# Lead-Halide Scalar Couplings in $^{207}$Pb NMR of APbX$_3$ Perovskites (A = Cs, Methylammonium, Formamidinium; X = Cl, Br, I)

M. Aebli[1,2], L. Piveteau[1,2], O. Nazarenko[1,2], B. M. Benin[1,2], F. Krieg[1,2], R. Verel[1]*, M. V. Kovalenko[1,2]*

[1]ETH Zürich, Department of Chemistry and Applied Biosciences, [2]Empa-Swiss Federal Laboratories for Materials Science and Technology, Dübendorf

Understanding the structure and dynamics of lead halide perovskites APbX$_3$ [A = Cs, methylammonium ($CH_3NH_3^+$, MA), formamidinium ($CH(NH_2)_2^+$, FA); X = Cl, Br, I] — has been a major research thrust. New insights were gained by using $^{207}$Pb solid-state nuclear magnetic resonance (NMR) spectroscopy at variable temperatures between 100 and 300 K [1]. The existence of scalar couplings $^1J_{Pb\text{-}Cl}$ of *ca.* 400 Hz and $^1J_{Pb\text{-}Br}$ of *ca.* 2.3 kHz could be confirmed for MAPbX$_3$ and CsPbX$_3$. Diverse and fast structural dynamics that include rotations of A-cations, harmonic and anharmonic vibrations of the lead-halide framework and ionic mobility affect the resolution of the coupling pattern. As a result, $^{207}$Pb NMR can be used to detect both structural disorder and phase transitions. Finally, by comparing bulk and nanocrystalline CsPbBr$_3$, it was confirmed that the PbBr$_6$-octahedra experience greater structural disorder at the nanoscale — a feature that cannot be readily captured by diffraction-based techniques.



[1] Marcel Aebli, Laura Piveteau, Olga Nazarenko, Bogdan M. Benin, Franziska Krieg, René Verel and Maksym V. Kovalenko, submitted, **2019**.

# Understanding how ligand substitution influences $CO_2$ adsorption in a series of sodalite-based MOFs

M. Asgari[1], R. Semino[2], P. A. Schouwink[1], I. Kochetygov[1], O. Trukhina[1], M. Ceriotti[2], W. L. Queen[1]*

[1]Institute of Chemical Sciences and Engineering, École Polytechnique Fédérale de Lausanne (EPFL)
CH-1051 Sion, Switzerland., [2]Institute of Materials, Ecole Polytechnique Fédérale de Lausanne,
1015 Lausanne, Switzerland.

Understanding structure-property relationships is essential for the rational design of Metal Organic Frameworks (MOFs) for $CO_2$ capture applications. In this work, we conduct a detailed study of the effect of structure on $CO_2$ adsorption properties of two highly crystalline families of frameworks, known as M-BTT and M-BTTri. While both structures consist of a sodalite type strucutre, their difference lies in the nature of the organic building block, a tetrazole versus a triazole, respectively. While Cu-BTTri exibits enhanced thermal and chemical stability, $CO_2$ adsorption capacities of Cu-BTTri are lower when compared to its isostructural counterpart, Cu-BTT. As such, i*n situ* synchrotron and neutron diffraction techniques were used to visualize the position and orientation of surface bound $CO_2$ in both materials. We find that the origin of their difference in performance arises from the higher electron donating effect of BTTri (triazole) ligand compared to the BTT (tetrazole); this difference makes the Jahn-Teller effect more pronounced in Cu-BTTri. In addition, variable temperature *in situ* diffraction measurements were employed to shed light on the structural changes of the $CO_2$-adsorbed Cu-BTTri framework as a function of temperature. Last, simulated breakthrough curves for both Cu-containing material were used to demonstrate the materials' performance in dry post-combustion $CO_2$ capture process. The separation potential, which takes into account both capacity and selectivity of the framework, predicts that Cu-BTT should outperform Cu-BTTri under dry post-combustion capture conditions. The information obtained in this work highlights the importance of various structural features on $CO_2$ adsorption.

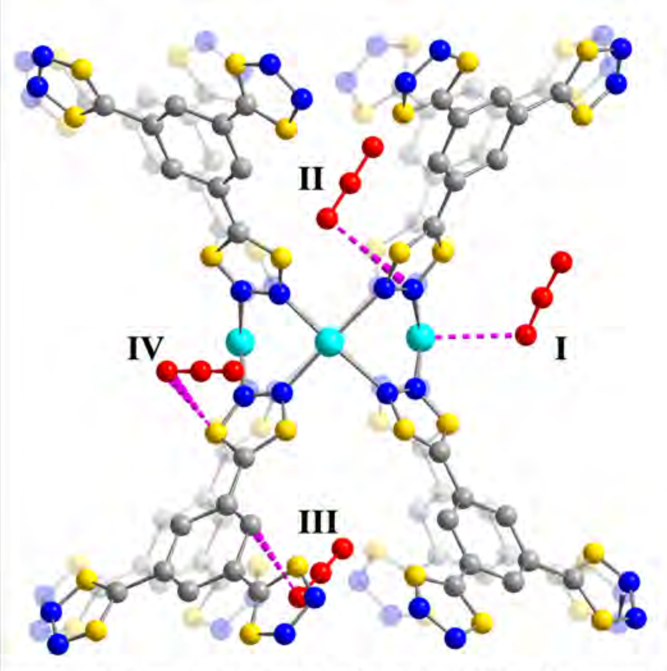


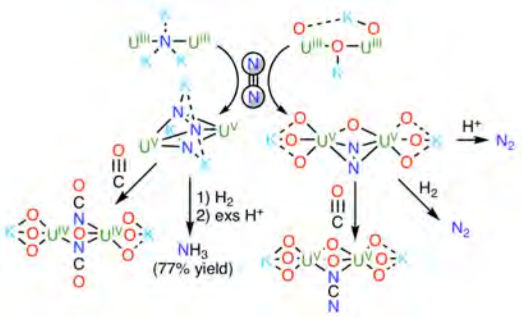
*Figure 1*- Ball and stick model of the Cu-BTTri framework dosed with 1.59 $CO_2$ per $Cu^{2+}$. The adsorbed $CO_2$ molecules are denoted as red spheres. Cu, C, N, are denoted as cyan, grey, and blue spheres, respectively. Hydrogen atoms have been excluded for the sake of clarity. Yellow spheres represent mixed sites containing both C and N. The pink dotted lines represent nearest neighbor interactions.

# Dinitrogen reduction and N-functionalization by uranium multimetallic complexes

L. Barluzzi[1], M. Mazzanti[1]*

[1]ISIC, École Polytechnique Fédérale de Lausanne (EPFL)

One of the most important and challenging tasks in modern chemistry is the reduction of dinitrogen and its transformation into ammonia ($NH_3$) or value-added N-containing organic compounds. In particular, uranium nitride materials (UN) have proven their activity as catalysts for the Haber-Bosch process which, combined with their potential application as nuclear fuels, attracted a large interest on their synthesis. Recently in our group, a multimetallic low valent uranium nitride complex was reported to perform the four-electron reduction of dinitrogen[1]. The reduced dinitrogen could also be functionalized or converted into ammonia. A new multimetallic low valent uranium complex able to perform the four-electron reduction of dinitrogen will be presented in this work. The different nature of the bridging ligand revealed to have major effects on the functionalization and the reactivity of the reduced dinitrogen[2].



When the reduction of dinitrogen is performed in presence of a reducing agent, bis(μ-nitride) complexes are reported as possible products. Despite that, functionalization of those complexes has never been achieved in uranium chemistry and is very rare in d-block chemistry. Moreover, uranium nitrides are also ideal target molecules for the investigation of magnetic communication between uranium atoms, whose examples remain limited. In this work, the synthesis of a bis(μ-nitride) uranium(V) and the functionalization of the nitride ligand with small molecules[3]is also presented, together with the investigation of its magnetic properties and the comparison with the ones of other uranium nitrides deriving from small molecule reactivity.

[1] M. Falcone, L. Chatelain, M. Mazzanti, *et al.*, *Nature*, **2017**, *547*, 332-335.
[2] M. Falcone, L. Barluzzi, M. Mazzanti, *et al.*, *Nature Chemistry,* **2019**, *11*, 154-160.
[3] L. Barluzzi, L. Chatelain, M. Mazzanti, *et al.*, *Chemical Science,* **2019**, *10*, 3543-3555.

# Towards fast and low-cost synthesis method of Prussian blue and its analogs - cathode materials for Na-ion batteries

D. Baster[1], W. Oliveira Da Silva[1], V. Costa Bassetto[1], H. Girault[1]*

[1]Laboratory of Physical and Analytical Electrochemistry, École Polytechnique Fédérale de Lausanne (EPFL) Valais Wallis, Rue de l'Industrie 17, Case Postale 440, CH-1951 Sion, Switzerland

Prussian blue - PB is an unique inorganic polycrystal with formal name iron (III) hexacyanoferrate (II) and empirical formula given by $Fe_4[Fe(CN)_6]_3$, which indicates the presence of the Fe(II) and Fe(III) in the complex compound. Whereas, the general chemical formula of Prussian blue analogs (PBAs) can be described as $A_xM[Fe(CN)_6]_y \cdot zH_2O$ ($0<x<2$; $0<y<1$), where A is an alkali metal ($Li^+$, $Na^+$, $K^+$) and M = Fe, Mn, Co, Ni, Cu. Prussian blue and its analogs possess a face-centered cubic structure *fcc,* having open ionic channels with diameters of about 0.32 nm and large interstitial "A" sites (≈ 0.46 nm).[1] Due to their 3D open framework and structural stability, hexacyanoferrates have recently attracted much attention as materials able to reversible insertion reaction of large alkali ions, such as $Na^+$ sodium-ion batteries. A typical way to obtain Prussian blue and its analogs is a co-precipitation synthesis at room temperature from an aqueous solution of a hexacyanoferrate (II) salt e.g. $K_4[Fe^{II}(CN)_6]$ mixed with an aqueous solution containing salt of transition metal on the +3 oxidation state, e.g. $FeCl_3$.[1] Electrochemical deposition from aqueous solutions could be also found as an useful method for producing thin film electrodes.[2] One of the successful and low-cost techniques of electrodes fabrication for various energy storage application is inkjet printing.[3] Print-light-synthesis has been successfully implemented in photovoltaic manufacturing and electronics industry. Print-light-synthesis is a new concept of obtaining materials using high-energy light in a very short period of time over a relatively large processing area for heating of thin film containing photosensitive precursor reaching temperatures of several hundred degrees centigrade.[3] A lot of effort has been put to develop printed batteries and printed materials for lithium-ion batteries have been investigated.[4] However, there is lack of information about printed electrodes for sodium-ion batteries.

In this work, we obtained PB and PBAs by novel Print-Light-Synthesis method and by well-known co-precipitation method. Comparison of the crystal structure and electrochemical behavior of materials synthesized using both methods was presented. On the basis of X-ray diffraction studies, it was revealed that Print-Light-Synthesis method allows to achieve well-crystalized, single-phase Prussian blue powder with cubic crystal structure (F*m*3*m* space group). The valance state of transition metals in Prussian blue and Prussian blue analogs was determined using X-ray photoelectron spectroscopy.

[1] M. J. Piernas Muñoz and E. Castillo Martínez, *Prussian Blue Based Batteries*, **2018**.
[2] P. Marzak, J. Yun, A. Dorsel, A. Kriele, R. Gilles, O. Schneider and A. S. Bandarenka, *J. Phys. Chem. C*, **2018**, 122, 8760–8768.
[3] A. Lesch, *Adv. Mater. Technol.*, **2018**, 3, 1–10.
[4| Y. Gu, A. Wu, H. Sohn, C. Nicoletti, Z. Iqbal and J. F. Federici, *J. Manuf. Process.*, **2015**, 20, 198–205.

# Low-dimensional tin-halides: properties and novel applications

B. M. Benin[1,2], S. Yakunin[1,2], D. N. Dirin[1,2], M. V. Kovalenko[1,2]*

[1]Laboratory of Inorganic Chemistry, Department of Chemistry and Applied Biosciences, ETH Zürich,
[2]Laboratory for Thin Films and Photovoltaics, Empa – Swiss Federal Laboratories for Materials Science and Technology

Newly discovered metal-halide based materials seldom adhere to a cubic, 3D perovskite structure, but rather adopt lower-dimensional structures with reduced connectivity between polyhedra. In the case of zero-dimensional (0D), fully disconnected, materials, a unique set of properties are observed.

One recent example is the fully-inorganic, perovskite-derived, $Cs_4SnBr_6$, which exhibits room-temperature, broad-band photoluminescence (PL) centered at 540 nm with a quantum yield of 15±5%.[1] This material also forms a compositional series $Cs_{4-x}A_xSn(Br_{1-y}I_y)_6$ (A = Rb, K; $x \leq 1$, $y \leq 1$) with PL that is tunable from 500-620 nm and a compositionally tunable Stokes shifts. Furthermore, these materials and other low-dimensional tin-halides such as $(C_4N_2H_{14}I)_4SnI_6$ and $[C(NH_2)_3]_2SnBr_4$ were all found to share an additional property – highly temperature-sensitive PL lifetimes.[2] These lifetimes are invariant to excitation power density, encapsulation, oxidation, spectral position, or other potential defects, and they are highly reproducible with a variation of *ca.* 40 picoseconds over the course of 50 consecutive measurements. With these highly reproducible and thermally ultra-sensitive lifetimes, cutting-edge remote optical thermography can be achieved with a thermometric precision of 13 mK.

[1] Bogdan M. Benin, Dmitry N. Dirin, Viktoriia Morad, Michael Worle, Sergii Yakunin, Gabriele Raino, Olga Nazarenko, Markus Fischer, Ivan Infante, Maksym V. Kovalenko, *Angew. Chem. Int. Ed. Engl.* **2018**, *57*, 11329-11333.
[2] Sergii Yakunin, Bogdan M. Benin, Yevhen Shynkarenko, Olga Nazarenko, Maryna I. Bodnarchuk, Dmitry N. Dirin, Christoph Hofer, Stefano Cattaneo, Maksym V. Kovalenko, *Manuscript Submitted* **2019**.

# $N_2$ coordination in $^{99}$Tc complexes

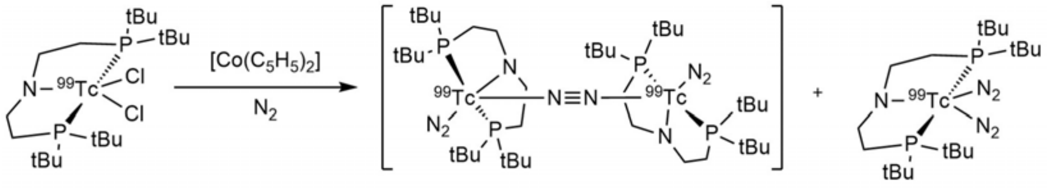
M. Besmer[1], H. Braband[1], R. Alberto[1]*

[1]University of Zurich, Department of Chemistry

The fixation of nitrogen into $NH_3$ is one of the most energy consuming industrial processes. The *Haber–Bosch* process produces ammonia from nitrogen and hydrogen gas. As a result of energy considerations and the high demand for ammonia for fertilizers and as feedstock for chemical synthesis, the search for alternatives to the *Haber–Bosch* process is still important.[1]

Novel approaches towards the splitting of $N_2$ were reported in the coordination sphere of rhenium complexes with a bulky pincer type ligand (PNP).[2,3] In this approach, the reduction of $N_2$ by the Re(I) center leads to the formation of a nitrido-rhenium(V) complex. Due to the extremely fast nitrido-complex formation, mechanistic studies of the splitting process turned out to be demanding. Following general trends in the periodic table, the lighter homologue of rhenium, technetium, is supposed to be less sensitive for Tc≡N formation, which should increase the possibility of isolating and characterizing intermediate structures of this nitrogen activation reaction.

Here we report the synthesis of $^{99}$Tc(III) complexes of the type [$^{99}$Tc(PNP)$Cl_2$] and their reactivities with $N_2$.



1 2 3

Under the same reaction conditions as applied for Re, new technetium(I) dinitrogen complexes form (**2** and **3**). These Tc(I) complexes have been isolated and structurally characterized. Dinitrogen complexes of technetium are rare, only two examples have been reported.[4,5] Therefore, these complexes **2** and **3** pave the way for a new class of low valent $^{99}$Tc compounds. Furthermore, they are potential mimics of the more reactive Re analogues, which will help to gain deeper insights into the $N_2$ splitting/activation mechanisms in the near future.

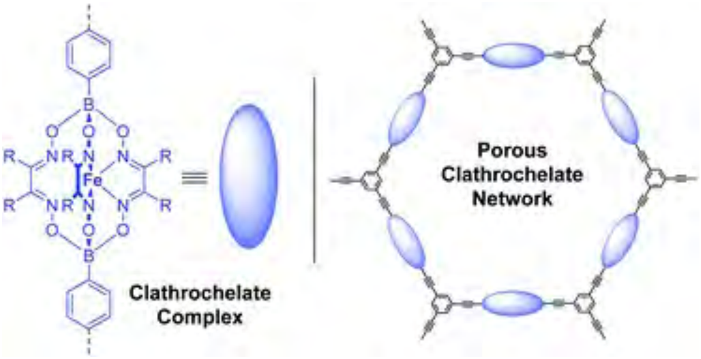
[1] H.-P. Jia, E. A. Quadrelli, *Chem. Soc. Rev.* **2014**, *43*, 547–564.
[2] I. Klopsch, M. Kinauer, M. Finger, C. Würtele, S. Schneider, *Angew. Chemie - Int. Ed.* **2016**, *55*, 4786–4789.
[3] I. Klopsch, M. Finger, C. Würtele, B. Milde, D. B. Werz, S. Schneider, *J. Am. Chem. Soc.* **2014**, *136*, 6881–6883.
[4] Y. T. Struchkov, A. S. Bazanov, L. Kaden, B. Lorenz, M. Wahren, H. Meyer, *Zeitschrift fur Anorg. und Allg. Chemie* **1982**, *494*, 91–97.
[5] A. K. Burrell, J. C. Bryan, G. J. Kubas, *J. Am. Chem. Soc.* **1994**, *116*, 1575–1576.

# Porous networks based on iron(ii) clathrochelate complexes

J. L. Bila[1], J. Pijeat[1], F. Fadaei-Tirani[1], R. Scopelliti[1], K. Severin[1]*

[1]ISIC, Ecole Polytechnique Fédérale de Lausanne (EPFL)

Microporous networks based on boronate ester-capped iron(ɪɪ) clathrochelate complexes are described. The networks were obtained by covalent cross-linking of tetrabrominated clathrochelate complexes *via* Suzuki–Miyaura polycross-coupling reactions with diboronic acids, or by Sonogashira–Hagihara polycross-coupling of clathrochelate complexes with terminal alkyne functions and 1,3,5-tribromobenzene. The networks display permanent porosity with apparent Brunauer–Emmett–Teller surface areas of up to $SA_{BET} = 593$ $m^2$ $g^{-1}$. A clathrochelate complex based on an enantiopure dioximato ligand was used to prepare chiral networks. One of these networks was shown to preferentially absorb ᴅ-tryptophan over ʟ-tryptophan.



*Severin et al., Dalton Trans.*, 2019, **48**, 4582-4588

# A multi-application-toolkit: one POM for water splitting, plastic waste recovery and anti-bacteria under light irradiation

H. Chen[1], G. R. Patzke[1]

[1]Department of Chemistry, University of Zurich

POMs, as one class of unique metal-oxo clusters with well-defined structures and nano size, are composed of W, Mo, V, Nb, and Ta centers with their highest oxidation states [1]. The unique redox activity, strong Brønsted acidity and unmatched range of molecular structures are key to the reactions that feature prominently in many applications [2]. They feature a remarkably wide application potential in the design of multifunctional POM materials with the ability to address different environmental issues, such as energy transformation, waste recovery, and sterilization of water [3–5]. At present, materials chemistry has evolved to the point where rational design of one multi-functional POM with synergistic capabilities is possible. Thus, designing a low-cost multi-application-POM will be undoubtedly promising.

[1] Xin Bao Han, Yang Guang Li, Zhi Ming Zhang, Hua Qiao Tan, Ying Lu, and En Bo Wang, *Journal of the American Chemical Society,* **2015**, 137, 5486–5493.
[2] Kevin P. Sullivan, Qiushi Yin, Daniel L. Collins-Wildman, Meilin Tao, Yurii V. Geletii, Djamaladdin G. Musaev, Tianquan Lian, and Craig L. Hill, *Frontiers in chemistry*, **2018**, 6, 365.
[3] Aleksandar Bijelic, Manuel Aureliano, and Annette Rompel, *Chemical communications,* **2018**, 54, 1153–1169.
[4] Xu, Lei; Yang, Xia; Guo, Yihang; Ma, Fengyan; Guo, Yingna; Yuan, Xing; Huo, Mingxin, *Journal of hazardous materials*, **2010**, 178, 1070–1077.
[5] Liu, Wei; Mu, Wei; Liu, Mengjie; Zhang, Xiaodan; Cai, Hongli; Deng, Yulin, *Nature Communications*, **2014**, 5, 3208.

# Colloidal Routes towards Highly-Monodisperse Intermetallic and Alloyed Nanocrystals

J. Clarysse[1], A. Moser[1], O. Yarema[1], M. Yarema[1], V. C. Wood[1]*

[1]ETH Zürich

Compounds containing two and more metals (i.e., intermetallic compounds and alloys) are ubiquitous from steel industry to precision engineering, from art works to cutting edge technologies such as state-of-the-art medical equipment. Intermetallic compounds combine the properties of the constituent metals and frequently exhibit synergistic effects, e.g. in the form of enhanced catalytic properties or lithium-ion battery anodes. Realizing intermetallic and alloyed compounds in form of nanoparticles broadens their functionality, exploiting e.g. high specific surface (i.e., catalysis), size-dependent properties (i.e., plasmonics and phase-change-based devices), and novel nanoscale phenomena (i.e., for magnetic nanomaterials), etc.

Despite these many interesting features the intermetallic nanoparticles offer, very few compositions have been reported in the literature thus far. Comparing to well-reported single component metallic nanoparticles, [1-2] the size and size distribution remain purely controlled for intermetallic nanoparticles. Synthesis procedures face the challenge of producing bimetallic nanoparticles in which metals with different reduction potentials need to be combined. On top of this compositional challenge, the synthesis should also allow control over reaction kinetics for two metal precursors, often exhibiting distinct reactivity differences in a given reaction medium.

In this work, we report a novel colloidal synthesis procedure which allows the synthesis of a range of bimetallic compositions (random alloys and intermetallic nanoparticles). Our synthesis procedure allows extensive control over the design of the intermetallic nanoparticles in terms of composition, size, size monodispersity, crystallinity, shape and surface chemistry. In addition, we observe interesting plasmonic properties for the synthesized intermetallic and alloyed nanoparticles. Figure 1 exemplifies highly-monodisperse intermetallic nanoparticles with the Au-Ga composition. [3]

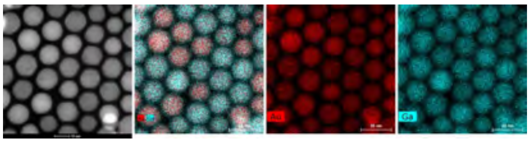


**Figure 1.** HAADF TEM image and STEM EDX mapping of highly monodisperse intermetallic nanoparticles of gold and gallium as an example of nanoparticles which can be synthesized using the new colloidal synthesis procedure. [3]

[1] M. Yarema et al., *J. Am. Chem. Soc.* **2014**, 136, 12422-12430.
[2] M. Yarema et al., *ACS Nano* **2012**, 6, 4113-4121.
[3] J. Clarysse et al., in preparation.

# Synthesis of two-dimensional zeolitic nanosheets for hydrogen sieving

M. Dakhchoune[1], K. V. Agrawal[1]*

[1]Institute of Chemical Sciences & Engineering (ISIC)

The synthesis of high-performance gas-sieving inorganic films by facile self-assembly of nanoporous building blocks is highly attractive and can address reproducibility and scale-up issues of inorganic membranes.[1,2] Highly crystalline two-dimensional zeolitic nanosheets are ideal for this attributing to their stability in harsh chemical and thermal conditions. In this talk, I will discuss successful exfoliation of sodalite precursor RUB-15 into crystalline nanometer-thick nanosheets hosting gas-sieving pore windows formed by rings of six silicate tetrahedra (Figure 1a-d). Ab-initio calculations confirm that these pores windows can efficiently sieve $H_2$ from $CO_2$ (Figure 1e). Thin films of exfoliated RUB-15, prepared by the hot-drop casting and vacuum filtration on porous ceramic substrate led to compact films, which demonstrated hydrogen sieving without requiring the secondary growth step, which is otherwise essential for the synthesis of zeolite membranes. $H_2/CO_2$, $H_2/N_2$, and $H_2/CH_4$ selectivities up to 13.2, 49.7 and 80.7 with a $H_2$ permeance of 1000 GPU, respectively, were achieved. Remarkable performance improvements were obtained by sealing non-selective pathways with a few nanometer-thick amorphous silica coating[3] ($H_2/CO_2$ and $H_2/N_2$, $H_2/CH_4$ selectivities up to 45 and 300, respectively, while $CH_4$ was completely rejected, Figure 1f). RUB-15 nanosheets-based membranes represent the first type of zeolite nanosheets capable of size-sieving light gases. Current efforts are aimed to test these membranes at temperatures higher than 130 °C to probe their performance in the real water-gas shift reaction conditions in the target to be exploited as membrane reactors.

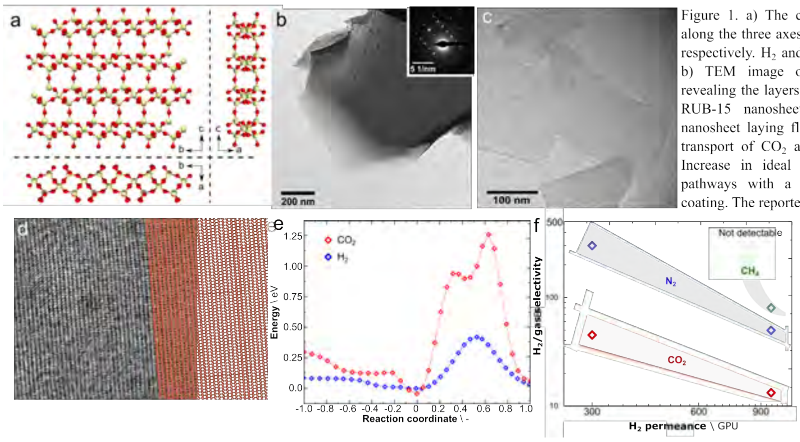


Figure 1. a) The crystal structure of single-layer RUB-15 along the three axes. Si and $O_2$ are shown in yellow and red, respectively. $H_2$ and interlayer guests are omitted for clarity. b) TEM image of an as-synthesized RUB-15 crystals revealing the layers of RUB-15. c) TEM image of exfoliated RUB-15 nanosheets. d) HR TEM image of RUB-15 nanosheet laying flat on the (0kl) plane. e) Energy for the transport of $CO_2$ and $H_2$ across the RUB-15 nanopore. f) Increase in ideal selectivities after sealing non-selective pathways with a few nanometer-thick amorphous silica coating. The reported data are at 90°C.

[1] M. Tsapatsis, *AIChE J.* **2014**, *60*, 2374–2381.
[2] J. Caro et al., *Microporous Mesoporous Mater.* **2008**, *115*, 215–233.
[3] S. Karimi, et al., *J. Memb. Sci.* **2015**, *489*, 270–274.

# Tris-diimine Fe$^{II}$ Spin Crossover Complexes Using Various N-Heterocyclic Ligands

N. Deorukhkar[1], T. Lathion[1], C. Besnard[2], L. Guénée[2], C. Piguet[1]*

[1]Dept. of Inorganic and Analytical Chemistry, University of Geneva, [2]Laboratory of Crystallography, University of Geneva

Fe$^{II}$ spin crossover (SCO) complexes, stimulated externally by temperature or light irradiation, have been extensively studied for their magnetic and optical properties. In these complexes, Fe$^{II}$(d$^6$) displays an equilibrium between the low spin ($^1A_{1g}$, $S = 0$, diamagnetic) and high spin ($^5T_{2g}$, $S = 2$, paramagnetic) configurations. The spin crossover process is controlled by the balance between the ligand-field splitting and the spin-pairing energy and remains essentially unpredictable as the various contributions to these factors are numerous and subtle (solvation, nature of the coordination bonds, induced local pressure).

In an effort to develop *tris*-diimine Fe$^{II}$ complexes displaying spin crossover properties in solution at room temperature, several asymmetric didentate units were investigated (Figure 1, Left, ligands **L1**-**L6**). By changing the number of nitrogen atoms or their position within the 6-membered *N* -heterocyclic part of the ligands, the spin transition can be finely tuned. Fe$^{II}$ complexes with unsymmetrical diimine ligands exist as a mixture of *facial* and *meridional* isomers in solution (Figure 1, right) for which different magnetic and optical properties are expected. The resultant spin crossover behaviour of the complexes therefore depends on the ratio of these two isomers and their respective magnetic properties.[1],[2]

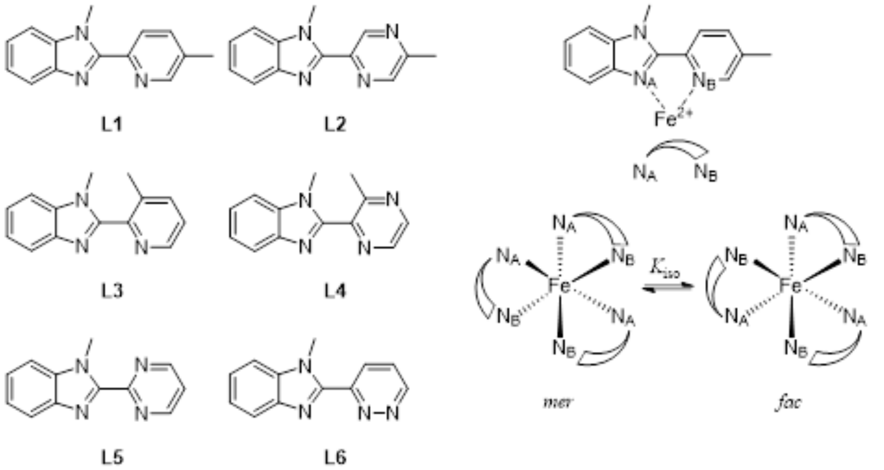


**Figure 1.** Left: investigated non-symmetrical *N*,*N*-diimine ligands. Right: *mer* ↔ *fac* equilibrium in solution.

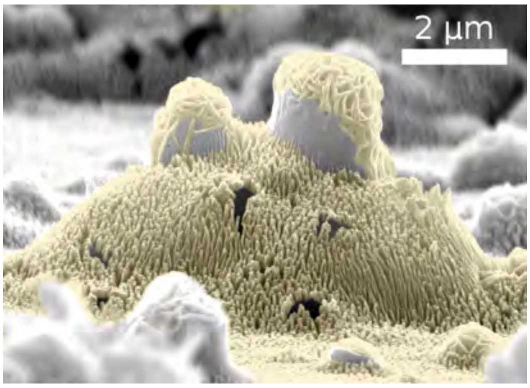
[1] Aboshyan-Sorgho, L.; Lathion, T; Guénée, L.; Besnard, C.; Piguet, C. *Inorg. Chem.* **2014**, *53*, 13093.
[2] Lathion, T.; Guénée, L.; Besnard, C.; Bousseksou, A.; Piguet, C. *Chem. Eur. J.* **2018**, *24*, 16873.

# Study of plasmon-enhanced water splitting in a hematite photoanode

L. Driencourt[1,2], B. Gallinet[1], S. Fricke[1], C. E. Housecroft[2], E. C. Constable[2]*

[1]CSEM, [2]Department of Chemistry, University of Basel

Solar water splitting can produce hydrogen gas from water through the electron transfer between an aqueous electrolyte and a semiconductor electrode [1]. Hematite (α-$Fe_2O_3$), can absorb a large part of the solar spectrum due to its appealing bandgap of about 2 eV. However, because of the poor charge transport properties of this material, an efficient photoanode needs to have nanoscale features such that most light is absorbed close to the semiconductor/electrolyte interface [2]. The quantity of light absorbed in a thin film of hematite can be further increased by including plasmonic nanostructures (Fig. 1) in the design of the electrode, due to their ability of confining the electromagnetic field over very small distances. This effect is studied theoretically with an analytical model and periodic electromagnetic simulations. A cost effective method for the fabrication of plasmonic substrates is demonstrated and its use for improving the efficiency of hematite photoanodes is studied experimentally.



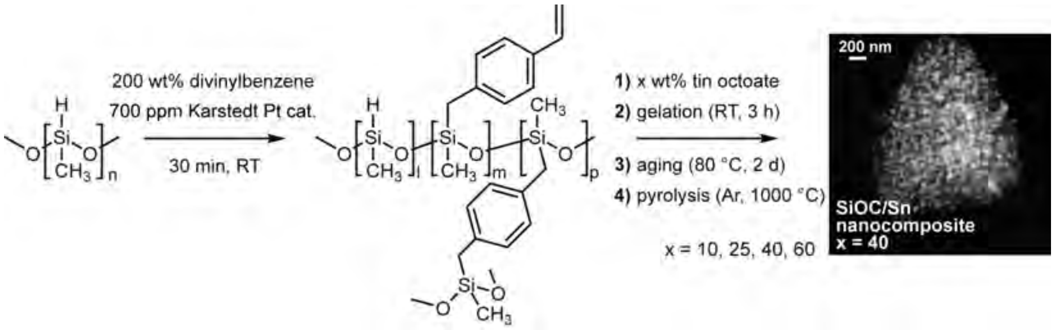
[1] M. Gratzel, *Nature*, **2001**, 414, 338–344
[2] A. G. Tamirat et al., *Nanoscale Horiz.*, **2016,** 1

# Silicon Oxycarbide - Tin Nanocomposite as a High-Power-Density Anode for Li-Ion Batteries

R. Dubey[1,3], P. Vallachira Warriam Sasikumar[2], F. Krumeich[1], G. Blugan[2], K. V. Kravchyk[1,3], T. Graule[2]*, M. V. Kovalenko[1,3]*

[1]Laboratory of Inorganic Chemistry, Department of Chemistry and Applied Biosciences, ETH Zürich, [2]Laboratory for High Performance Ceramics, Empa, [3]Laboratory for Thin Films and Photovoltaics, Empa

Due to the huge volume changes occurring upon lithiation of Sn, obtaining a stable electrochemical performance of Sn-based anodes for Li-ion batteries remains a formidable challenge. The prevailing approaches towards stabilization of such electrodes invoke embedding of Sn in the form of nanoparticles (NPs) in an active/inactive matrix. The latter helps to buffer the volume changes of Sn, impart electrical contact and prevent particle aggregation upon its lithiation/delithiation. Among all matrices, silicon oxycarbide (SiOC) appears to be an ideal choice, combining inter alia good electrical conductivity and high intrinsic capacity. [1] However, a homogeneous dispersion of Sn NPs within SiOC has not been reported until now. [2] We report a facile synthesis of 5-30 nm Sn NPs exceptionally homogeneously embedded in SiOC matrix via the pyrolysis of a functionalized preceramic polymer. [3]



Anodes comprising SiOC/Sn nanocomposite demonstrate high capacities of 644 mAh $g^{-1}$ and 594 mAh $g^{-1}$ at current densities of 74.4 and 744 mA $g^{-1}$ (C/5 and 2C rates for graphite anode), respectively, and show excellent rate capability. The mechanism of lithiation/de-lithiation of SiOC/Sn nanocomposite and its morphological changes have been assessed by *in-situ* powder X-ray diffraction and *ex-situ* transmission electron microscopy measurements. Finally, full cells have been tested, which demonstrate the potential of SiOC/Sn at areal capacities relevant for high-power industrial applications.

[1] C. Stabler et al., *J. Am. Ceram. Soc.*, **2018**, 101, 4817-4856.
[2] J. Kaspar et al., *Adv. Funct. Mater.*, **2014**, 24, 4097-4104.
[3] R. Dubey et al., **2019**, *submitted.*

# Can an Oxidized Zinc Finger Bind Zinc? Reversible Oxidation of Zinc fingers

M. Durtschi[1], S. Johannsen[1], R. O. Sigel[1]*

[1]University of Zurich, Department of Chemistry B

Zinc finger (ZnF) domains are one of the most physiologically relevant examples of metalloproteins, as they are present in about 3% of all genes in the human genome. They are part of transcription factors that regulate diverse processes such as transcription, translation, or apoptosis. Beyond these roles, ZnF proteins can also act as redox switches, sensing the cell redox status and triggering appropriate responses. This is possible because Zn(II)-coordinating cysteine residues are readily oxidized, leading to dissociation from the stabilizing Zn(II) ion along with loss of structure and loss of DNA-binding activity.

In order to efficiently act as regulatory transcription factors under normal physiological conditions, ZnFs need to associate but also to dissociate readily from DNA. However, no dissociation mechanism is currently known. Dissociation under simultaneous Zn(II) release seems unlikely, since the level of free Zn(II) in the cell is virtually zero and no Zn(II) chaperones are known, and since one-time use of ZnFs would be highly inefficient. We therefore hypothesize that the dissociation of ZnFs from DNA involves oxidation-induced formation of an alternative structure in which Zn(II) remains bound. Thus, subsequent reduction, of the ZnFs would easily restore its DNA-binding activity.

Our central aim is to prove the existence of such an oxidized Zn(II)-binding structure under physiological conditions and to characterize it by NMR and X-ray crystallography. The structural role of alternative Zn(II) ligands is of particular interest, and can be directly addressed if the structure is characterized. Similar oxidized Zn(II)-binding structures have been shown to exist e.g. in the nucleocapsid protein of HIV-1[1], and in *in vitro* oxidized ZnF models[2], although the latter involves the formation of sulfinate moieties, which might not be formed *in vivo*. Overall, this study is of fundamental interest in obtaining a structural and mechanistic understanding of the dissociation process of zinc fingers in general, and of their function as redox switches in particular.

Financial support by the University of Zurich is gratefully acknowledged.

[1] L. Yu, Y. Hathout, C. Fenselau, R.C. Sowder, L.E. Henderson, W.G. rice, J. Mendeleyev, E. Kun, *Chem. Res. Toxicol.* **1995,** 8, 586-590.
[2] Lebrun, A. Tron, C. Lebrun, J.-M. Latour, N. D. McClenaghan, O. Sénèque, *Chemistry* **2015,** 21, 14002-14010.

# Unprecedented uranium species: from water-stable uranyl(V) to uranium(IV) POM clusters.

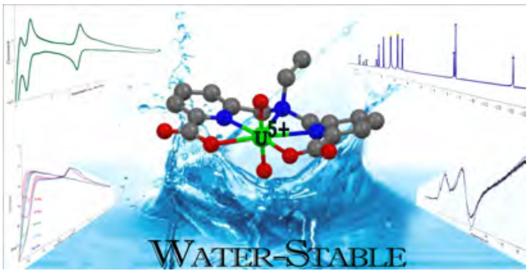
R. Faizova[1], L. Chatelain[1], R. Scopelliti[1], F. Fadaei-Tirani[1], M. Mazzanti[1]*

[1]ISIC, École Polytechnique Fédérale de Lausanne (EPFL)

Traditionally pentavalent uranyl has been thought of as a highly unstable species of limited environmental importance because of the tendency of aqueous U(V) to disproportionate under most Eh-pH conditions. However, in the past decade, it has been demonstrated that uranyl(V) is a persistent intermediate in the biological and abiotic transformation of soluble uranyl(VI) compounds into insoluble uranium(IV) species ($UO_2$ or U(IV) discrete clusters). In particular, U(V) is often found in association with Fe-containing minerals such as goethite and magnetite. Besides the importance of this process for ground-water remediation, the role of U(V) remains unclear as there is no appropriate synthetic model to perform the required studies.

The first example of stable uranyl(V) complex in organic media was reported more than 10 years ago, inspiring very fast development in the field, but none of the reported compounds have shown stability in aqueous media at environmentally relevant pH.

We will present the synthesis of the first uranyl(V) complex that is stable in both organic and aqueous media. This was achieved by using an aminopicolinate ligand, combining the pentadentate binding mode with the ability to form stable complexes with metal ions in water. [1] Additionally, the effect of $Fe^{2+}$ on the stability of U(V) toward proton induced disproportionation and redox reactions was investigated. Cation-cation interaction between uranyl(V) oxygen and $Fe^{2+}$ was shown to be essential for the stabilization of U(V).[2] The formation of discrete uranium(IV) clusters of various nuclearities (U6 – U38) and the time dependence of the assembly of uranium oxo clusters in hydrolytic conditions will also be presented.[3]



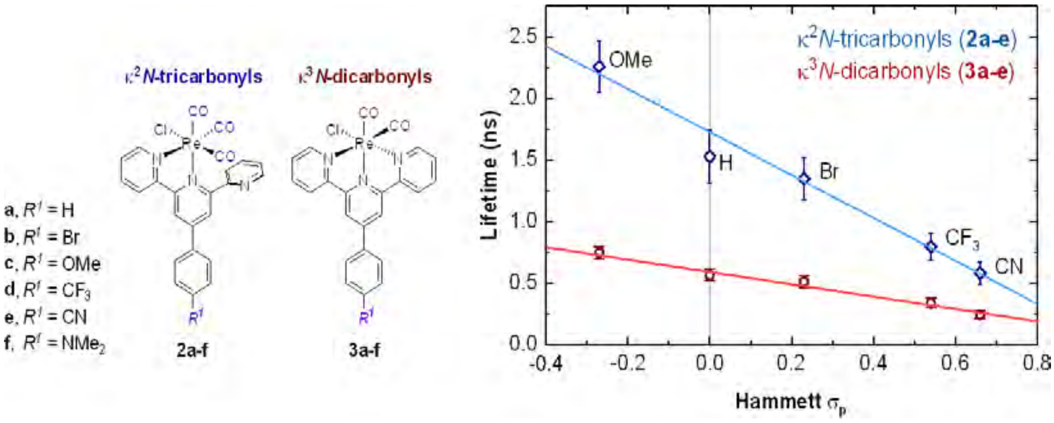
[1] R. Faizova, R. Scopelliti, A.-S. Chauvin, M. Mazzanti, *J. Am. Chem. Soc.,* **2018**, *140*, 13554.
[2] R. Faizova, S. White, R. Scopelliti, M. Mazzanti, *Chemical Science*, **2018**, 9, 7520–7527.
[3] L. Chatelain, R. Faizova, F. Fadaei-Tirani, J. Pécaut, M. Mazzanti, *Angewandte Chemie International Edition*, **2019**, 58, 3021–3026.

# Re(I) $\kappa^2$N-tricarbonyl and $\kappa^3$N-dicarbonyl complexes with terpyridine ligands: unusual substituent effects and photocatalytic properties

R. J. Fernández-Terán[1], L. Severy[1], D. Tilley[1], P. Hamm[1]

[1]Department of Chemistry, University of Zürich

The ground- and excited-state properties of six Re(I) $\kappa^2$*N*-tricarbonyl and six $\kappa^3$*N*-dicarbonyl complexes with 4’-(4-substituted-phenyl)-terpyridine ligands bearing substituents of different electron donating abilities were evaluated. Significant modulation of the electrochemical potentials and $^3$MLCT lifetimes were observed when going from CN to OMe (Figure 1).



With the more electron-donating NMe$_2$ substituent, a dramatic enhancement of the lifetime (from ca. 2.5 ns to ca. 380 ns) results from the change in the character of the lowest triplet excited state, which shifts from $^3$MLCT to $^3$ILCT. These observations were absent in their corresponding $\kappa^3$*N*-dicarbonyl counterparts, which relax instead to a $^3$MLCT state. The characters and signatures of all these excited states were determined by ultrafast transient IR spectroscopy ranging from femto- to microseconds, and were evaluated theoretically with the help of DFT calculations and IR spectroelectrochemistry. Selected complexes were also evaluated as photosensitizers for homogeneous hydrogen production, with the $\kappa^2$*N*-NMe$_2$ complex resulting in a stable and efficient photocatalytic system, reaching TON$_{Re}$ values of over 2100.

[1] R. Fernández-Terán, L. Sévery, S. D. Tilley, P. Hamm, **2019**, *submitted.*

# Functionalised Boronate Ester-Capped Helicates

E. Giraldi[1], K. Severin[2]*

[1] École Polytechnique Fédérale de Lausanne (EPFL), 1015 Lausanne, Switzerland., [2]École Polytechnique Fédérale de Lausanne (EPFL), 1015 Lausanne, Switzerland.

Clathrochelate complexes have been extensively used in supramolecular chemistry and material science; they are very stable and inert complexes with intriguing proprierties.[1] Half-clathrochelate complexes are formed by condensation of 2-pyridine aldoxime with a boronic acid in the presence of a metal(II) salt (M(II) = Fe, Zn or Mn). These new complexes are more labile than classical clathrochelates: they are capped by one boronate ester cap and the metal ion is not completely encapsulated. By changing the oxime ligand, $M_2L_3$ helicate-like complexes have been obtained. A library of boronate ester-capped helicates have been developed from linear dioxime ligands with 2-pyridine aldoxime connected by varying numbers of p-xylene spacers (n = 0, 1).[2] Both half-clathrochelate and helicate complexes have been found to scramble the boronate esters cap and to exchange the metal centre from Mn(II) to Zn(II) upon addition of $Zn(OTf)_2$. The functionalisation of boronate ester-capped helicates with pyridinylboronic acids make them suitable metalloligands for the obtainment of large assemblies in combination with Pd or Pt salts. Moreover, the oxime ligands could further be tailored upon extension of the linear spacers between the two 2-pyridinealdoxime group to obtain structures with larger cavities suitable for guest encapsulation.

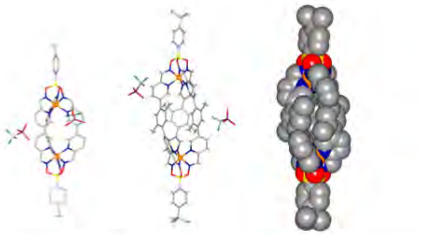


**Figure:** X-ray characterization of boronate ester-capped helicates with Fe(II) as metal centre.

[1] S. M. Jansze and Kay Severin, *Acc. Chem. Res***., 2018**, *51*, 2139-2147.

[2] N. Ousaka, S. Grunder, A. M. Castilla, A. C. Whalley, J. F. Stoddart, J. R. Nitschke, *J. Am. Chem. Soc*., **2012**, *134*, 15528-15537.

# Oxygen functionalization of carbon molecular sieve membranes to modulate pore-size-distribution for gas separation

S. Huang[1], K. V. Agrawal[1]*

[1]Laboratory of Advanced Separations (LAS), École Polytechnique Fédérale de Lausanne (EPFL)

Carbon molecular sieves (CMS) films, prepared by controlled pyrolysis of polyimdies, possess slit-like nanopores. Such nanopores can sieve molecules based on their size, and a sub-angstrom resolution in molecular differentiation can be achieved depending upon the polymer chemistry and the pyrolysis conditions.[1-3] Å tunable modulation of the pore-size-distribution (PSD) by chemical functionalization of the carbon framework is highly attractive. However, such functionalization, typically in presence in traces of oxygen, has been only demonstrated only at a high temperature (>500 ºC) increasing the sophistication of the membrane fabrication.

In this talk, I will demonstrate a straightforward and highly tunable oxygen functionalization using a pulsed ozone treatment at room temperature on 100-nm-thick CMS film (Fig. 1a), yielding attractive gas separation performance.[4] Carbonyl groups and epoxy groups were grafted on CMS backbone as confirmed by X-ray photoelectron spectroscopy (Fig. 1b). He, $H_2$, $CO_2$, and $CH_4$, with the kinetic diameter in the range of 0.255 – 0.38 nm, were used as probe gases to monitor the evolution of PSD. After ozone treatment, gas selectivity could be improved by several folds, primarly induced by the narrowing of the electron-density-gap in the slits like pores in CMS by a fraction of an angstrom as a result of oxygen functionalization. For example, $H_2/CH_4$ and $H_2/CO_2$ selectivities increased from 13.3 to 50.7, and from 1.8 to 7.1, respectively (Fig.1c). The functionalization chemistry is easy to implement and is expected to be adopted widely.

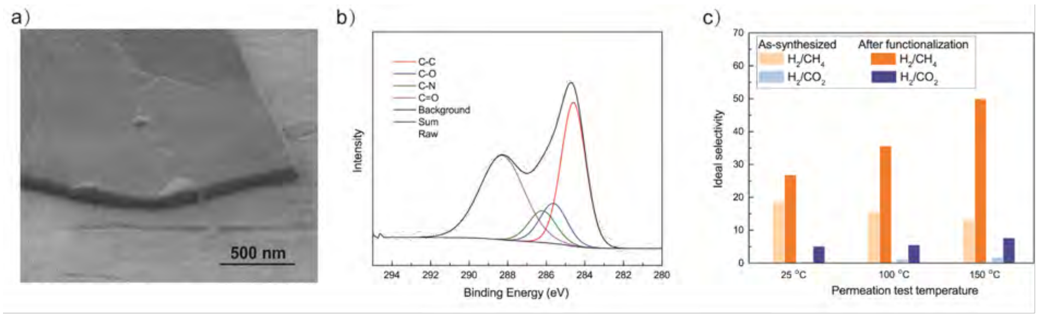


Fig. 1. a) Cross-section SEM image of a 100nm-thick CMS film. b) XPS spectra from the oxygen functionalized CMS film. c) Gas selectivity of CMS membranes before and after the ozone treatment.

[1] Rungta, M.; Wenz, G. B.; Zhang, C.; Xu, L.; Qiu, W.; Adams, J. S.; Koros, W. J. *Carbon,* **2017**, 115, 237–248.
[2] Adams, J. S.; Itta, A. K.; Zhang, C.; Wenz, G. B.; Sanyal, O.; Koros, *Carbon,* **2019**, 141, 238–246.
[3] Koh, D.-Y.; McCool, B. A.; Harry W., D.; Ryan P., L. *Science.* **2016**, 353.
[4] Huang, S.; Villalobos, L.F.; Babu, D. J.; He, G.; Li, M.; Züttel. A.; Agrawal, K. V. *ACS Appl. Mater. Interfaces*, **2019**, 11, 16729-16736.

# Synthesis of nanopores in graphene lattice with a sub-angstrom resolution

S. Huang[1], K. V. Agrawal[1]*

[1]Laboratory of Advanced Separations (LAS) École Polytechnique Fédérale de Lausanne (EPFL)

Graphene lattice is atom thick, ideally suited for high-performance size-sieving of molecules. However, the honeycomb lattice of graphene is impermeable to even the smallest of the molecules, and one has to etch vacancy-defects (nanopores) in graphene.[1-3] The state-of-the-art etching chemistries neither self-limiting nor easy to control, and as a result, a narrow pore-size-distribution (PSD), needed to differentiate molecules with high-efficiency has not been reported. Common etching techniques lead to wide PSD which results in a poor molecular selectivity. Since a high porosity in graphene is desired to maximize the molecular flux, it is highly attractive to develop a controllable etching chemistries that maximizes porosity while yielding an optimal PSD. In this talk, I will discuss an ozone-based etching chemistry which was regulated by homemade millisecond reactor. With the millisecond-etching reactor, controllable and rapid ozone etching on graphene lattice was achieved, where the concentrated etching medium generated high-density pore nucleation, while minimized the pore expansion due to the short time. $H_2$, $CO_2$, $N_2$, and $CH_4$, with the kinetic diameter in the range of 0.289 – 0.38 nm, were used as probe gases to monitor the evolution of PSD. Overall PSD with resolution of 0.3 nm would be etched leading to extremely attractive separation performance with $CO_2$ permeance of 2626 GPU and $CO_2/CH_4$ selectivity of 20 and $CO_2/N_2$ selectivity over 20 (Fig.1). Such methods will accelerate the development of high-performance membranes for the carbon capture.

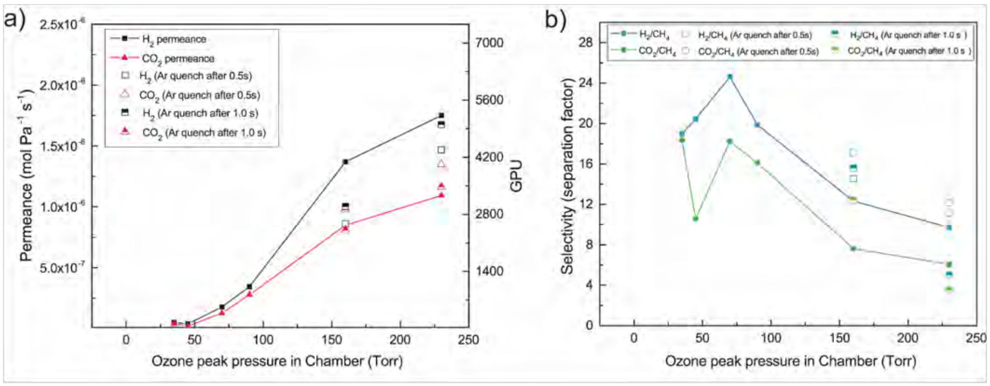


Fig. 1. Gas separation performance of graphene membranes with different rapid high-temperature ozone treatments

a) gas permenace of $H_2$ and $CH_4$. b) Ideal selectivity (separation factor) of $H_2/CH_4$ and $CO_2/CH_4$.

[1] Wang, L.; Boutilier, M. S. H.; Kidambi, P. R.; Jang, D.; Hadjiconstantinou, N. G.; Karnik, R. *Nature Nanotechnology*, **2017**, 12, 509–522.
[2] Huang, S.; Dakhchoune, M.; Luo, W.; Oveisi, E.; He, G.; Rezaei, M.; Zhao, J.; Alexander, D. T. L.; Züttel, A.; Strano, M. S.; Agrawal, K. V. *Nature Communications* **2018**, 9, 1–11.
[3] Zhao, J.; He, G.; Huang, S.; Villalobos, L. F.; Dakhchoune, M.; Bassas, H.; Oveisi, E.; Agrawal, K. V. *Science Advances* **2019**, 5, eaav1851.

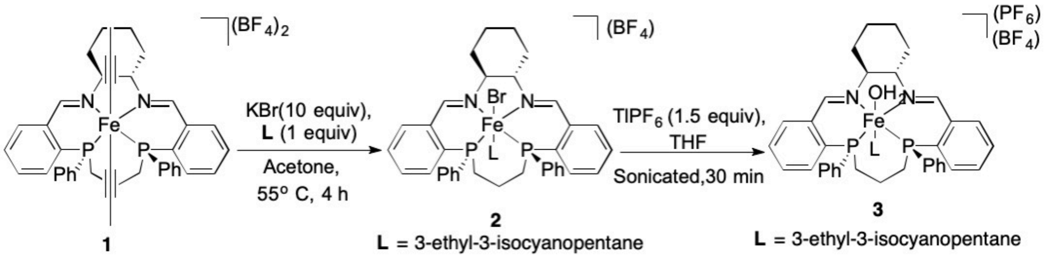
# $N_2P_2$ Macrocyclic Iron(II) Catalysts for the Asymmetric Cyclopropanation of Alkenes

H. Jayaprakash[1], A. Mezzetti[1]*

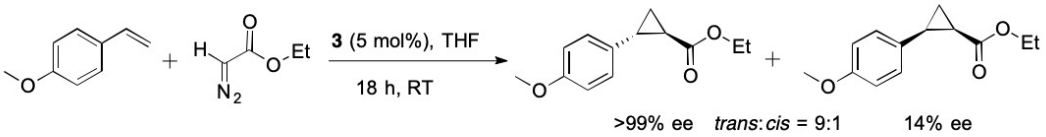
[1]ETH Zürich

The asymmetric iron-catalyzed cyclopropanation of alkenes has been studied with tetraphenylporphyrin,[1] and bisoxazolines,[1] but no phosphine ligands have been tested. Phosphine ligands are of special interest due to their ability of chiral induction and easy synthesis.

We report here the first intermolecular asymmetric cyclopropanation of activated alkenes with a chiral Fe(II) $N_2P_2$ macrocyclic catalyst.[2] Complex **1** was treated with KBr (10 equiv) and ligand **L** (1 equiv, acetone, 55° C, 4 h) to obtain the bromoisonitrile derivative **2**. The active catalyst **3** was prepared via bromide abstraction from **2** with $TlPF_6$ (1.5 equiv, THF, sonication, 30 min).



Catalyst **3** (5 mol%, THF, RT, 18 h) cyclopropanates 4-methoxystyrene upon slow addition of ethyl diazoacetate (1 equiv) over 6 h to give the *trans* cyclopropane as the major product and as single enantiomer in 35% yield.The optimization, substrate scope, and mechanistic studies are in progress so as to compare its behavior with the ruthenium complexes with open chain PNNP ligands that have been previously prepared in our group.[3]



[1] (a) Ingmar Bauer, Hans-Joachim Knölker, *Chem. Rev,* **2015**, *115*, 3170. (b) Guodong Du, Bruno Andrioletti, Eric Rose, Keith Woo, Organometallics, **2002**, *21*, 4490. (c) Jun-Jie Shen, Shou-Fei Zhu, Yan Cai, Huan Xu, Xiu-Lan Xie, Qi-Lin Zhou, *Angew. Chem,* **2014**, *53*, 1.
[2] Raphael Bigler, Raffael Huber, Marco Stöckli, Antonio Mezzetti, *ACS Catal,* **2016**, *6*, 6455.
[3] (a) Stephan Bachmann, Maya Furler, Antonio Mezzetti, *Organometallics* **2001**, *20*, 2102. (b) Cristina Bonaccorsi and Antonio Mezzetti, *Organometallics* **2005**, *24*, 4953.

# DNA-bis(benzene)iron based mechanophores

E. Jean-Pierre[1], E. Janett[1], C. G. Bochet[1]*, K. M. Fromm[1]*

[1]University of Fribourg, Chemistry department

Since many years, researchers are interested in sandwich-type complexes that can be used in various areas like in organic catalysis or in industry for the production of pharmaceutical falvours, in agrochemical... Recently, we have shown that ferrocene can be used as mechanophore, hence as preferential breaking point in polymers such as polyurethane[1].

In this project, we decided to use bis(benzene)iron[2] associated to a linker[3] allowing to fix it to DNA. Embedding such an entity into a polymer is expected to give rise to a two-step mechanophore[4] in which first the H-bonds of DNA, and then the sandwich-complex are cleaved as increasing force is exerted. Mismatches in DNA pairing can tune the mechanical strength of the mechanophore.

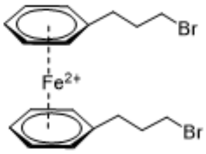


Figure: Bis(benzene)iron molecule

[1] Michela Di Giannantonio, Mathieu A. Ayer, Ester Vester-Sesto, Marco Lattuada, Christoph Weder, Katharina M. Fromm, *Angew.Chem.Int. Ed.*, **2018**, 57,11445 –11450.
[2] D. Jones, L. Pratt, G. Wilkinson, *J. Chem. Soc*., **1962**, 4458-4463.
[3] Marco Couto, Ignacio Mastandrea, Mauricio Cabrera, Pablo Cabrela, Francesc Teixidor, Hugo Cerecetto, Clara Viñas, *Chem. Eur*., **2017**, 23, 9233-9238.
[4] Jun Li, Chikkannagari Nagamani, Jeffrey S. Smore, *Acc. Chem. Res*., **2015**, 48 (8), 2181–2190.

# Carbon Dioxide Insertion Reactions Driven by Electron-Rich Uranium(IV) Complexes Supported by Tridentate Non-Innocent Ligands

N. Jori[1], M. Falcone[1], R. Scopelliti[1], M. Mazzanti[1]*

[1]Institut des Sciences et Ingénierie Chimiques, Ecole Polytechnique Fédérale de Lausanne (EPFL)

With the aim of performing multi-electron redox transformations, there is a growing interest in the synthesis of coordination compounds with non-innocent redox ligands. These ligands can cooperate with the metal center in the redox activity of complexes, because they act as electron reservoirs and transfer these electrons to different substrates.[1] In particular for uranium, which commonly performs one-electron transfer, the possibility of storing extra electrons in the ligand can open new pathways in its redox activity towards the small molecule activation.

Polydentate Schiff bases are convenient and synthetically versatile candidates. Tetradentate Schiff base ligands, through the reversible formation and cleavage of C-C bonds, can act as electron reservoirs and source, respectively.[2] A tridentate ligand, the trensal can be useful to synthesize unsaturated U(III) compounds with potential small molecule activation.

In this work we report the synthesis, structural properties and reactivity of the bis-U(IV) trensal complex, which is capable of insert $CO_2$ and the reduced cyclic species formed by reaction with stoichiometric amount of $KC_8$shows not only $CO_2$ insertion, but also scission and formation of carbonate.

[1] Volodymyr Lyaskovskyy, Bas de Bruin, ACS Catalysis, **2012,** *2* (2), 270-279

[2] Julie Andrez, Valentin Guidal, Rosario Scopelliti, Jacques Pécaut, Serge Gambarelli, Marinella Mazzanti, *J. Am. Chem. Soc.,* **2017**, 139, 25, 8628-8638

# Selective $CO_2$ capture from Automobile exhausts using polyethylene imine impregnated mesoporous silica.

A. Justin[1], W. L. Queen[1]*

[1]Institute of Chemical Sciences and Engineering, LFIM

Increasing $CO_2$ level in the atmosphere became one of the major environmental concerns leading to global warming and negatively impacting the ecosystem. Growth of countries' economies cause alarming $CO_2$ emissions due to impetuous industrialization and uncontrolled increase of a number of automobiles. The composition of gas mixtures from an automobile exhaust is known as $CO_2/O_2/N_2$ = 18/10/72% and the material having high $CO_2$ capacity and selectivity at 0.15 bar is believed to help in mitigating this issue. In this report, we designed and synthesized composite materials based on porous silica with polyethylene imine (PEI) with 600 average molecular weight, which was selected as one of the most efficient reagents able to capture $CO_2$ at low pressures thanks to an increased number of primary and secondary amines therein. Further, we demonstrated the importance of accessible mesopores of the selected type of silica to achieve high PEI loading (50wt %) which afforded a superior $CO_2$ capacity. Increasing the pore size and pore volume from 6.8 nm and 0.93 $cm^3/g$ for silica SBA-15 to 10.8 nm and 1.3 $cm^3/g$ for silica KIT-6, $CO_2$ uptake enhanced from 1.6 mmol/g to 2.2 mmol/g at $40^oC$ and 1 bar. We used Temperature Swing Adsorption (TSA) method in TGA to study $CO_2$ working capacity of the material on continuous adsorption desorption cycles. By screening $CO_2$ performance in our composites at three different desorption temperatures, we found no complete desorption at $100^oC$, whereas $CO_2$ react with amines to form cyclic urea at $150^oC$ and linear urea formation at $120^oC$. Finally, we developed a mild regeneration procedure to assure a complete desorption of the captured $CO_2$ from our composite to avoid a chemisorption-type secondary processes occurring mainly on primary amines of polymer aliphatic chains by converting to secondary amines by epoxybutane (EB) to form EB-PEI. 64wt% EB-PEI KIT-6 silica composite showed a constant $CO_2$ capacity of 1.5 mmol/g over 40 cycles at 1 bar. This composite indeed showed same $CO_2$ capacity in a saturated humid (100% RH) stream as well. We further utilized breakthrough study on this material to quantify the adsorption selectivity and performance under 15%$CO_2$ and 85% $N_2$ mixture, as well as under 80% RH.

# RNA folding of a group II intron investigated by single molecule FRET under various Magnesium(II) concentrations using TIRM and confocal microscopy

K. Kraft[1], S. Zelger-Paulus[1], R. Börner[1], R. O. Sigel[1]*

[1]Department of Chemistry, University of Zurich

Group II introns are a class of self-splicing ribozymes and belong to the largest ribozymes in nature [1]. They fold into their native structure in a stepwise process, yet $Mg^{2+}$ dependent manner [2]. For studying the folding mechanism, the model system D135-L14, derived from the group II intron *Sc*.ai5γ of *Saccharomyces cerevisiae* is widely used. The construct possesses all necessary domains (D) for catalytic activity and has two additional loops (L) for labelling with fluorescence dyes, thus suitable for single-molecule Förster resonance energy transfer (smFRET). Previous studies assumed an overall compaction of the construct from the unfolded to the native state [2-4]. To further investigate the folding process, we developed a new construct eD135-L14e that comprises the two flanking exons labelled with fluorescence dyes [2,5]. Hence, together with L1 and L4 labelling this enables various FRET and distance trajectories to study the folding in a comprehensive manner [5]. So far smFRET studies have been carried out at a $Mg^{2+}$ concentration of 100 mM only. To determine the FRET network, i.e., the combination of multiple FRET trajectories to attribute distinct FRET values of different labelling positions to the same conformational state, smFRET experiments under various $Mg^{2+}$ concentrations will be performed. We assume, that FRET histograms will change and reveal and the magnesium(II) dependent population of conformational states ranging from the unfolded to the native fold of the ribozyme. The Cy3/5 labelled construct is investigated using both total internal reflection microscopy (TIRM) and confocal microscopy smFRET to ensure data integrity on all time scales. With the FRET network at hand, we will be able to solve the dynamic pathway from the pre- to the post catalytic state of the ribozyme.

Financial support by the University of Zurich is gratefully acknowledged.

[1] Chen Zhao, Anna Marie Pyle, Trends in Biochem, **2017**,42 (6), 470-482.
[2] Miriam Steiner, Krishanthi S. Karunatilaka, Roland K.O. Sigel, David Rueda, Natl. Acad. Sci. U.S.A., **2008**, 105 (46), 13853-13858.
[3] Krishanthi S. Karunatilaka, Amanda Solem, Anna Marie Pyle, David Rueda, Nature, **2010**, 467 (7318), 935-939.
[4] Bishnu P. Paudel, Erica Fiorini, Richard Börner, Roland K.O. Sigel, David S. Rueda, Natl. Acad. Sci. U.S.A., **2018**, 115 (47), 11917-11922.
[5] Anita G. Schmitz, Susann Zelger-Paulus, Gilles Gasser, Roland K.O. Sigel, ChemBioChem, **2015**, 16 (9). 1302-1306.

# A comparison of radiolabeling methods for iron oxide nanoparticles

J. Lamb[1], J. P. Holland[1]*

[1]University Zurich, Department of Chemistry, Winterthurerstrasse 190, Zurich, 8057, Switzerland

Nanoparticles have emerged as valuable scaffolds for the development of multimodal imaging agents. Superparamagnetic iron oxide nanoparticles (SPIONs) exhibit shortened $T_2$relaxation times can be modified with a radioisotope, allowing them to act as potential positron emission tomography/magnetic resonance imaging (PET/MRI) agents. Classically, the radiolabelling of nanoparticles often relies on chemical modification with prosthetic groups or radiometal ion chelates. Although feasible, these methods can have adverse effects on the pharmacokinetic profile of the nanoparticles *in vivo*. To circumvent this problem, recent efforts led the development of a chelate-free, intrinsic radiolabelling of SPIONs.[1]In this work, we compare the radiolabeling efficiencies of classical and intrinsic methods using Fereheme® (FH); an FDA cleared SPION-based MRI contrast agent consisting of an iron oxide core with a carbohydrate coating.

FH was modified using (3-aminopropyl)triethoxysilane (APTES) which introduced a free amine for further modification. Dynamic light scattering analysis showed that modification had little effect on the size of the particles (36.3±0.5 nm *versus*control 29.9±0.3 nm). The amine content was determined colourimetrically to be 31.5 µmol per mg of nanoparticle. The free amine then acted as a handle to attach a photochemically active [$^{68}$Ga]GaDOTA-PEG$_4$-ArN$_3$complex, allowing for light-initiated photoradiolabelling of the nanoparticle under illumination at 365 nm with a radiochemical conversion efficiency of 4.1±0.4% (Figure 1). In spite of the low radiolabelling efficiency our data confirm that photoradiochemical methods can be combined with nanoparticles. The intrinsic, surface labelling indicated that FH could be easily radiolabelled with $^{68}$Ga$^{3+}$ions without the use of chelate with radiochemical conversions and purities >95% (*n*=3).[2]These high radiochemical conversions and rapid radiolabeling kinetics indicate that the chelate-free approach based on surface radio-mineralisation of the nanoparticle core is a superior technique in comparison to both established chemistries and recent photochemical conjugation methods.

J.P.H thanks the Swiss Cancer League (Krebsliga Schweiz; KLS-4257-08-2017), the Swiss National Science Foundation (SNSF Professorship PP00P2_163683), the European Research Council (ERC-StG-2015, NanoSCAN – 676904), and the University of Zurich for financial support.

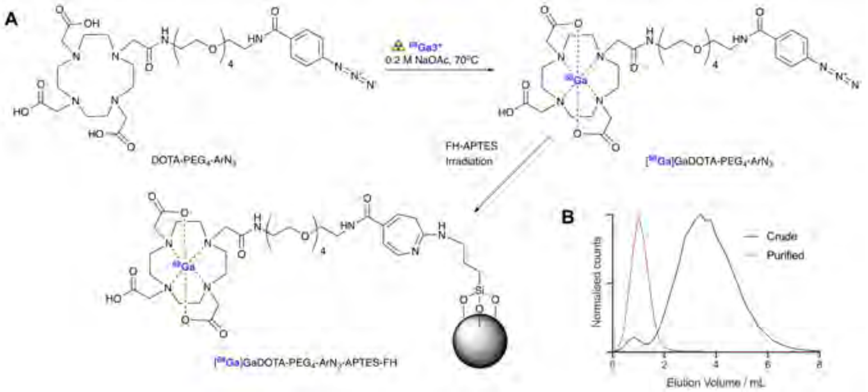


Figure 1: A) Synthesis of the [$^{68}$Ga]GaDOTA-PEG$_4$-ArN$_3$-APTES-FH B) Analytical PD-10-SEC elution profiles of the [$^{68}$Ga]GaDOTA-PEG$_4$-ArN$_3$-APTES-FH crude reaction mixture *vs.*the purified construct.

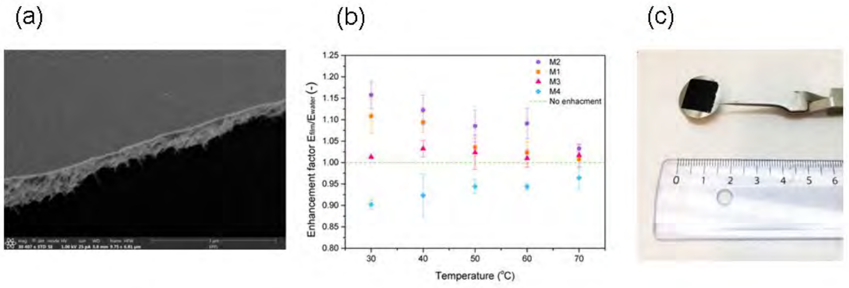
[1] J. Lamb and J. P. Holland, *J Nucl Med*, 2018, **59**, 382–390.
[2] E. Boros, A. M. Bowen, L. Josephson, N. Vasdev and J. P. Holland, *Chem. Sci.*, 2015, **6**, 225–236.

# Enhancement in liquid-vapor phase transition kinetics of water upon confinement under graphene nanopores

W. Lee[1], K. V. Agrawal[1]*

[1]Laboratory of Advanced Separations (LAS), Ecole polytechnique fédérale de Lausanne (EPFL)

The confinement at nanoscale leads to interesting physical and chemical effects, often deviating from behavior described by the classical theories [1, 2]. In particular, evaporation of fluids from nanopores plays an important role in natural as well as industrial processes. Control of such processes can be promising for energy-efficient applications such as steam generation [3] from waste heat. However, it is challenging to precisely create a confining geometry with controlled sub-nanometer dimensions. In this talk, I will discuss the synthesis of single-layer graphene film hosting nanopores spanning in size from 0.3 nm to several nanometer. I will further discuss our attempts to elucidate the water evaporation behavior (liquid-vapor transition) at the nanoscale. The free-standing membrane has a hierarchical structure (Fig. 1a) composed of graphene, nanoporous carbon and carbon nanotubes layers that facilitate efficient liquid transport to liquid-vapor interface at nanopores, and thus enables the study the interfacial evaporation kinetics. The preliminary results showed that water evaporates faster with the presence of graphene membrane compared to that without (Fig. 1b), and it has been revealed that the evaporation enhancement is correlated with pore size. Meanwhile, large-area graphene films (area up to 53 mm$^2$) were engineered for the future applications that exploit the fast evaporation phenomenon (Fig. 1c).



[1] Agrawal, K. V.; Shimizu, S.; Drahushuk, L. W.; Kilcoyne, D.; Strano, M. S., *Nature Nanotechnology* **2016,** *12*, 267.
[2] Hummer, G.; Rasaiah, J. C.; Noworyta, J. P., *Nature* **2001,** *414* (6860), 188-190.
[3] Ni, G.; Li, G.; Boriskina, Svetlana V.; Li, H.; Yang, W.; Zhang, T.; Chen, G., *Nature Energy* **2016,** *1*, 16126.

# Superconductivity in the η-carbide-type oxides $Zr_4Rh_2O_x$

K. Ma[1], J. Lago[1,2], F. O. von Rohr[1]*

[1]Department of Chemistry and Department of Physics,University of Zurich, CH-8057 Zürich, Switzerland, [2]Department of Inorganic Chemistry, Univ. del Pais Vasco (UPV-EHU), 48080 Bilbao,Spain

**Keywords: intermetallics, η-carbides, superconductivity**

A promising approach for superconductivity has been the exploration of layered or cage structured compounds with interlayer space or void positions that can be occupied with additive elements as electron dopants (see, e.g., references [1-3]). Here, we report on the synthesis and the superconductivity in $Zr_4Rh_2O_x$ ($x$ = 0.4, 0.5, 0.6, 0.7, 1.0). These compounds crystallize in the η-carbide structure, which is a filled version of the complex intermetallic $Ti_2Ni$ structure. We find that in the system $Zr_4Rh_2O_x$, already a small amount ($x \geq 0.4$) of oxygen addition stabilizes the η-carbide structure over the more common intermetallic $CuAl_2$ structure-type, in which $Zr_2Rh$ crystallizes. We show that $Zr_4Rh_2O_{0.7}$ and $Zr_4Rh_2O$ are bulk superconductors with critical temperatures of $T_c \approx 2.8$ K and 4.7 K in the resistivity, respectively. Our analysis of the superconducting properties reveals both compounds to be strongly type-II superconductors with critical fields up to $\mu_0 H_{c1}(0) \approx 8.8$ mT and $\mu_0 H_{c2}(0) \approx 6.08$ T. Our results support that the η-carbides are a versatile family of compounds for the investigation of the interplay of interstitial doping on physical properties, especially for superconductivity.

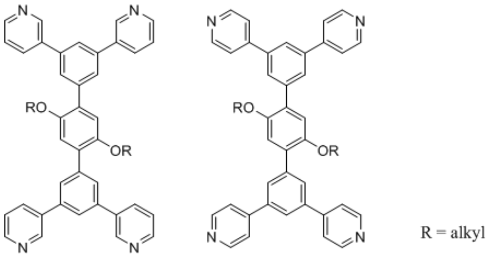
[1] H. Hosono et al. *Phil.Trans. R.Soc.,* A373, 20140450 (2015).
[2] E. Morosan, *et al.*, *Nature Physics* 2, 544 (2006).
[3] Y. Zhang, *et al.*, *npj Quantum Materials* 2, 45 (2017).

# Tetratopic bis(3,2':6',3"-terpyridines) and bis(4,2':6',4"-terpyridines): two different isomers for the synthesis of 3D coordination networks

G. Manfroni[1], F. Baca[1], Y. M. Klein[1], A. Prescimone[1], E. C. Constable[1]*, C. E. Housecroft[1]*

[1]Department of Chemistry, University of Basel

New tetratopic bis(3,2':6',3''-terpyridine) and bis(4,2':6',4''-terpyridine) ligands have been prepared and characterized. The different flexibilities of the two isomers with respect to N-donor directionality is affected in one case, but not in the other, by rotation about the inter-pyridine ring C–C bonds. Their role in the design and structure of coordination networks derived from reactions with $Co(NCS)_2$ will be discussed and compared.



# Silver-Induced Alpha-Helix Formation from Random-Coiled Peptide

F. Marquenet[1], L. Babel[1], V. Chabert[1], K. M. Fromm[1]*

[1]Fromm Group, Department of Chemistry, University of Fribourg, Chemin du musée 9 CH-1700 Fribourg, Switzerland.

Three-dimensional conformation is an important parameter of a molecule’s structure. The structure of a molecule can induce a particular role as well as an information storage[1]. This is why researchers try to understand the design of self-organized systems called foldamers. One such possible foldamer structure is the α-helix[2]. For a protein, it consists of the self-assembly of amino acids (AA) into a helix composed of 3.6 residues/turn.

The SilE protein is a protein of the silver efflux pump and believed to absorb and release silver acting as a sponge. We could previously show that this capacity is due to the presence of both methionine and histidine residues[3, 4], acting as ligands for silver ions in a linear mode, thus inducing the formation of an α-helix (Figure 1). Indeed, we synthesized a model peptide, excerpt from SilE, which has an amorphous structure until it self-organizes upon addition of silver ions due to the coordination with methionine and histidine residues.

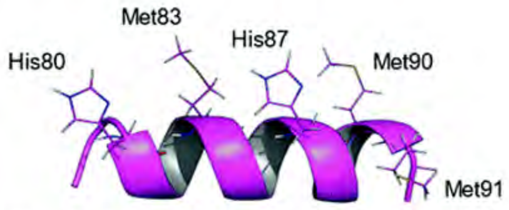


**Figure 1.** SilE model peptide self-organizing into an α-helix in presence of silver.[3]

[1] Samuel H. Gellman, *Acc. Chem. Res.* **1998**, 31, 173-180.
[2] Claire M. Grison, Jennifer A. Miles, Sylvie Robin, Andrew J. Wilson, David J. Aitken, *Angew. Chem. Int. Ed.* **2016**, 55, 11096-11100.
[3] Valentin Chabert, Maggy Hologne, Olivier Sénèque, Olivier Walker, Katharina M. Fromm, *Angew. Chem. Commun.* **2018**, 54, 10419-10422.
[4] Valentin Chabert, Maggy Hologne, Olivier Sénèque, Aurélien Crochet, Katharina M. Fromm, *Angew. Chem. Commun.* **2017**, 53, 6105-6108.

# Chaperone-mediated crystallization of the early cysteine-labeled protein ($E_c$-1)

A. Marquez Espinoza[1], E. Freisinger[1]*

[1]Department of Chemistry, University of Zurich, Switzerland

In general, metallothioneins (MTs) are ubiquitous small, cysteine-rich proteins that are mostly important for Zn(II) and/or Cu(I) homeostasis as well as heavy metal detoxification. The early cysteine-labeled protein ($E_c$-1) from *Triticum aestivum* (bread wheat) embryos was the first MT from higher plants to be isolated and characterized [1]. Spectroscopic data including structure determination with NMR spectroscopy showed that $E_c$-1 is a two-domain protein that can coordinate six Zn(II) ions via cysteine and histidine ligands.[2-4]. However, as NMR spectroscopy is only able to give indirect information about metal ion coordination, and on top, as most of this indirect information is based on experiments using the $^{113}$Cd nucleus as a mimic for Zn(II), additional structural data from crystallography is highly desirable. As previous trials with the full-length protein as well as its separate domains were not successful, we present here our first attempts of crystallization mediated by chaperones. Glutathione s-transferase (GST) or the maltose-binding protein (MBP) is used to provide an additional surface area to promote crystal contact formation [5]. We already obtained several crystals of fusion-proteins that could provide complementary information of the $E_c$-1 architecture to understand its biological functions. In addition, this approach could be extended to others MTs with intrinsically disordered regions that prohibit structural investigations even with NMR spectroscopy.

Financial support from the Swiss National Science Foundation and the Faculty of Science of the University of Zurich is gratefully acknowledged.

[1] Lane, R. Kajioka, T. Kennedy, *Biochem. Cell Biol.*, **1987,** 65, 1001-1005.
[2] I. Leszczyszyn, R. Schmid, C. Blindauer, *Proteins,* **2007,** 68, 922-935.
[3] E.A. Peroza, R. Schmucki, P Güntert, E. Freisinger, O. Zerbe, *J. Mol. Biol.*, **2009,** 387, 207-218.
[4] Loebus, E.A. Peroza, N. Blüthgen, T. Fox, W. Meyer-Klaucke, O. Zerbe, E. Freisinger, *J. Biol. Inorg. Chem.*, **2011,** 16, 683-694.
[5] Kobe, T. Ve, S.J. Williams, *Acta Cryst. F Struct. Biol. Commun.*, **2015,** 71, 861-869.

# Ruthenium Complexes with Substituted Pincer-type PYA Ligands for Increased Activity in Transfer Hydrogenation Catalysis

P. Melle[1], J. Thiede[1], D. Hey[2], M. Albrecht[1]*

[1]Department für Chemie & Biochemie, Universität Bern, Freiestrasse 3, 3012 Bern, Switzerland, [2] Fakultät für Chemie, Technische Universität München, Lichtenbergstraße 4, 85748 Garching, Germany

Ligand systems that offer flexibility and assist the metal in catalytic bond making and breaking have recieved much attention recently.[1] Pyridylidene amide (PYA) ligands have been shown to be electronically flexible N-donor sites and have sucessfully been used for transfer hydrogenation catalysis.[2,3] Here we present a new series of ruthenium complexes bearing *para*-substituted PYA pincer ligands (Figure 1). Analytic studies revealed a substantial influence of the substituents on the electronic properties of the metal centre. These complexes showed improved catalytic activity in transfer hydrogenation of ketones. Further optimization strategies afforded a most active precatalyst which features a 10fold increase of catalytic activity compared to the unsubstituted reference complex, reaching turnover frenquencies of more than 20,000 h$^{-1}$ under a low catalyst loading of 0.1 mol%.

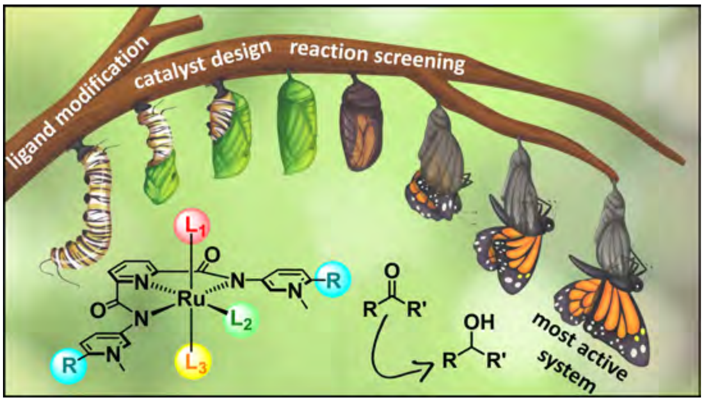


**Figure 1**. Ligand modification, catalyst design and reaction screening of ruthenium complexes bearing *para*-substituted PYA ligands for improved activity in transfer hydrogenation catalysis.

[1] R. Khusnutdinova, D. Milstein, *Angew. Chem. Int. Ed.* **2015**, 54, 12236-12273.
[2] P. Melle, Y. Manoharan, M. Albrecht, *Inorg. Chem.* **2018**, 57, 11761-11774.
[3] P. Melle, M. Albrecht, *Chimia* **2019**, 73, 299-303.

# Can high-quality single-layer graphene be really synthesized at low temperature?

M. Moradi[1], M. H. Khan[1], K. V. Agrawal[1]*

[1]Laboratory of Advanced Separations (LAS) Institute of Chemical Sciences & Engineering (ISIC)
École Polytechnique Fédérale de Lausanne (EPFL)

The synthesis of high-quality single-layer graphene is of paramount interest for a number of applications spread across disciplines in chemistry, physics, material sciences and engineering. We are highly interested in utilizing intrinsic defects in graphene lattice for size-sieving of molecules.[1] Based on studies of other materials, we postulate that the nature of intrinsic defects are a function of the crystallization temperature and the composition of the carbon precursor. So far, only methane has been used as a precursor to synthesize high-quality single-layer graphene hosting a small density of intrinsic defects.[2] Such synthesis is usually carried out at 1000 ºC.

Inspired by the recent reports on the synthesis of graphene at low temperature (up to 100 ºC on Cu foil) using benzene as the precursor,[3] we systematically studied the temperature-dependent growth and defect density of benzene-derived graphene. Our results were surprising and in stark contrast with these reports. In this talk, I will demonstrate that single-layer graphene cannot grow at temperature below 700 ºC. I will further establish that earlier reports were likely misled by the presence of the unintentional benzene residues in the growth chamber, which then leads to graphene crystallization during the preparation stage of the catalytic Cu foil (pre-annealing at 1000 °C). By carefully purging the reactor before the pre-annealing step, we confirm that only amorphous carbon is deposited below 700 °C. Finally, we report that high-quality single-layer graphene can be synthesized above 825 °C by using benzene as growth precursor. The synthesized graphene sheet contains a small density of intrinsic defects. Using gas transport experiments, we report that these defects are smaller than 0.38 nm. The membrane made of these graphene single-sheets showed an attractive $H_2$ sieving ($H_2$ permeance over 2000 gas permeation units; $H_2/C_3H_8$ and $H_2/SF_6$ selectivities of 12 and 50, respectively).

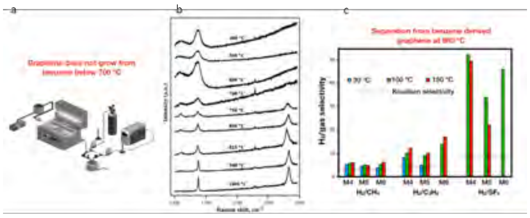


Figure 1: A schematic of the setup for the synthesis of single-layer graphene using benzene precursor (a). Raman spectra of benzene-derived graphene sheets at various growth temperatures (400-1000 °C) (b). Corresponding gas selectivities of the graphene membranes with respect to $H_2$ (c).

[1] Jiang, D., et al., *Nano Lett.,* **2009**, 9, 4019-4024.
[2] Celebi, K., et al., Science, **2014**, 344, 289-292.
[3] Huang, S., et al., *Nat. Sommun,* **2018**, 9, 2632.
[4] Jang, J., et al., *Sci. Rep.,* **2016**, 5, 17955.
[5] Li, Z., et al., *ACS. Nano.,* **2011**, 5, 3385-3390.

# Plant MT3 proteins: The unpredictable MT family

M. Perinelli[1], E. Freisinger[1]*

[1]University of Zurich

Metallothioneins (MT2) are a super-family of small metalloproteins that can be found in any living organism. They are characterized by a considerable high amount of cysteine residues (up to 30% of all amino acids), which give these proteins an extraordinary binding capacity for soft transition metal ions. The plant MT3 subfamily has been under investigation for a long time, in particular the mus_MT3 form from *Musa acuminata* (banana). Mus_MT3 features two cysteine-rich domains, N- and C-terminus, that bind one or two metal ions ($Cd^{II}$ and $Zn^{II}$ were investigated), respectively, and, due to the presence of a cysteine-free linker, are able to close up to allow for a single cluster conformation with four metal ions in total.[1,2] Besides this interesting rearrangement ability, the MT3 subfamily presents two semi-conserved position for histidine residues: 46 and 65, both located in the C-terminal region with 65 representing the terminal amino acid.[3]

In order to study the cluster formation and the role of the histidine residues, different members of this subfamily have been studied, either as the full-length protein or focusing on the separate C-terminus: mal_MT3 from apple featuring two histidine (46 and 65) and fra_MT3 from strawberry, which is devoid of any histidines. For comparison, the N65H_mus_MT3 mutant was also prepared and investigated and contains two histidine residues as mal_MT3. The proteins have been characterized with different spectroscopic techniques in order to evaluate their binding capacity. To our great surprise, it was observed that the presence of the additional histidine in mal_MT3 and N65H_MusMT3 rather inhibits single cluster formation completely than assisting or enhancing the binding capacity in the presence of $Zn^{II}$ as predicted. Both, $Co^{II}$ titrations and 2D-heteronuclear NMR, have been used to understand if the histidines have a role in metal binding and which interactions are responsible for the cluster formation.

*Project funding by Swiss National Science Foundation to EF is gratefully acknowledged.*

[1] E. Freisinger, *Inorg. Chim. Acta*, **2007**, 360, 369-380.
[2] E. Freisinger, *J. Biol. Inorg. Chem.*, **2011,** 16, 1035-1045.
[3] A. C. S. Cabral, J. Jakovleska, A. Deb, J. E. Penner-Hahn, V. L. Pecoraro and E. Freisinger, *J. Biol. Inorg. Chem.*, **2018,** 23, 91–107.

# Installing a metal active centre in peptide scaffolds through an unnatural NHC-amino acid

M. Planchestainer[1], K. Lenzen[1], F. Paradisi[2,1], M. Albrecht[1]

[1]Departement für Chemie und Biochemie, Universität Bern, [2]School of Chemistry, University of Nottingham

We have recently obtained evidence that replacing a histidine in a mutant of *Pseudomonas aeruginosa*azurin,[1]a small T1-type copper protein, with an extraneous N-heterocyclic carbene (NHC) ligand markedly facilitates redox processes.[2]We have then expanded our consideration to the nitrite reductase (NiR) from *Alcaligenes faecalis*, an active enzyme with an azurin-like T1 copper centre and the ability to catalyse the reduction of nitrite to nitric oxide.[3]Although the activity was lower than the WT NiR, the mutant H145G rescued with NHC showed a three-fold increase compared to imidazole as exogenous ligand.

In light of these results, we developed a synthetic route to access a Fmoc-protected histidinium salt, precursor of a NHC binding amino acid, to deliver a novel metal coordination motive in peptide backbones for the generation of artificial enzymes. It was then successfully incorporated into various peptide sequences through solid-phase peptide synthesis (SPPS) and functionalised with $IrCl_2Cp^*$. We will discuss synthetic aspects as well as the catalytic activity of these peptide NHC complexes in hydrogenation with a particular focus on the influence of nearby amino acids in this artificial active site.

[1] M. Planchestainer, N. Segaud, M. Shanmugam, J. McMaster, F. Paradisi and M. Albrecht, *Angew. Chemie Int. Ed.*, **2018**, 10677–10682.
[2] M. Melaimi, M. Soleilhavoup and G. Bertrand, *Angew. Chemie - Int. Ed.*, **2010**, 49, 8810–8849.
[3] Y. Li, M. Hodak and J. Bernholc, *Biochemistry*, **2015**, 54, 1233–1242.

# Precise etching of nanopores in single-layer graphene

M. Rezaei[1], K. V. Agrawal[1]*

[1]Laboratory of Advanced Separations (LAS), Institute of Chemical Sciences & Engineering (ISIC),
École Polytechnique Fédérale de Lausanne (EPFL)

Graphene membranes have the potential to exceed the permeance and selectivity limits of conventional gas separation membranes in various fields including natural gas purification, hydrogen recovery, and carbon capture[1,2]. However, a precise control of the pore size distribution and achieving a high pore-density has been the biggest bottleneck in realizing their full capacity. Recent efforts in introducing selective pores in graphene has been led to either wide pore size distribution (PSD), due to simultaneous pore nucleation and expansion of the existing pores), or low density of pores, hindering the true potential of this material[3,4]. To overcome this issue, we utilizing a clean mild etchant to expand the defects in graphene, nucleated by $O_2$-plasma or other techniques, without introducing new defects in graphene basal plane in a precise and scalable manner, thus keeping the desired narrow PSD.

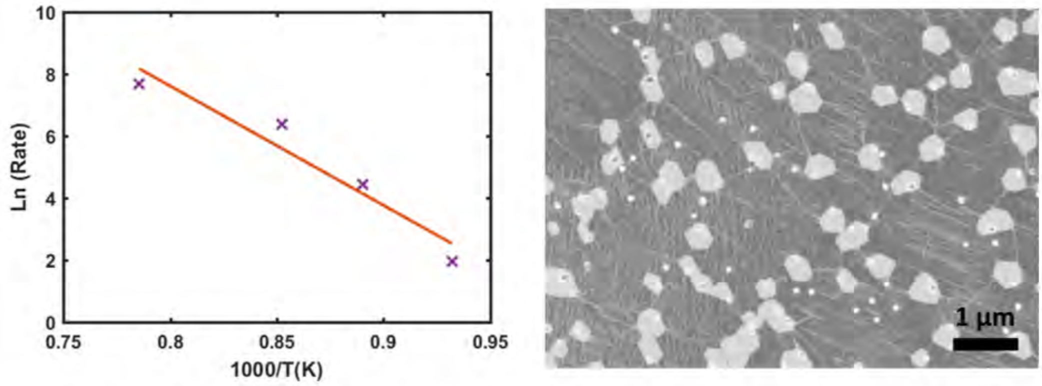


*Figure 1. Left) linear behavior of the natural logarithm of the etching rate versus the reciprocal of the etching temperature at 500 mTorr $CO_2$. Right) SEM image of the expanded pores (lighter areas) in graphene (darker areas) by $CO_2$ on Cu.*

Among the surveyed options, $CO_2$ is the most promising gas for etching the graphene edges at high temperatures without introducing new defects in the pristine graphene lattice[5]. This is also confirmed in our experiments by scanning electron microscopy (SEM) and Raman analysis. Presence of bond disorders and functional groups at the edges of the chemical vapor deposited (CVD) graphene results in the higher chemical reactivity of the edge carbon atoms compared to the perfectly bonded $sp^2$ carbon atoms in the basal plane. Moreover, a correlation based on Arrhenius expression is developed to estimate the precise value of the temperature- and $CO_2$ concentration-dependent etching rate, and the activation energy of 320 kJ/mol is measured. By tuning the etching condition, it is possible to accurately control the etching rate down to 1 nm/min. To the best of our knowledge, this is the first clean and controllable etching technique that avoids the wide PSD due to nucleating new pores while expanding the existing ones. This method can be used to achieve the desired pore size for various separation applications based on the sieving principle.

[1] Wang, L., et al., *Nature Nanotechnology*, **2017**, 12, 509-522.
[2] Dutta, S., et al., *Scientific Reports*, **2019**, 9, 5202.
[3] Surwade, S.P., et al., *Nature Nanotechnology*, **2015**, 10, 459-464.
[4] Zhao, J., et al., *Science Advances*, **2019**, 5, 1851.
[5] Yang, R.T. and Duan, R.Z., *Carbon*, **1985**, 23(3), 325-3

# 2,2'-Bipyridine Ligands in Copper(I)-based dyes for Dye-sensitized Solar Cells: Does a spacer make it better?

G. Risi[1], C. E. Housecroft[1]*, E. C. Constable[1]*

[1]Department of Chemistry, University of Basel

The dye sensitized solar cell (DSC) which was first reported in 1991[1] is a cheap and relatively simple constructed device. It is a promising source from which to obtain cost effective and sustainable solar energy.

In our research group we develop Cu(I)-based dyes which are composed of an anchoring and an ancillary ligand.[2] The latter is tuned according to the desired photochemical/structural properties. Many are based on the 2,2'-bipyridine (bpy) scaffold, the π-system of which is extended by introducing substituted phenyl rings in the 4,4'-positions of the bpy unit.

In this investigation we compare the properties of some 4,4'-disubstituted bpy ligands with their corresponding derivatives bearing a spacer between the main scaffold and the phenyl rings. The ligands are characterised as well as their homoleptic Cu(I) complexes, and the performances tested in DSCs devices.

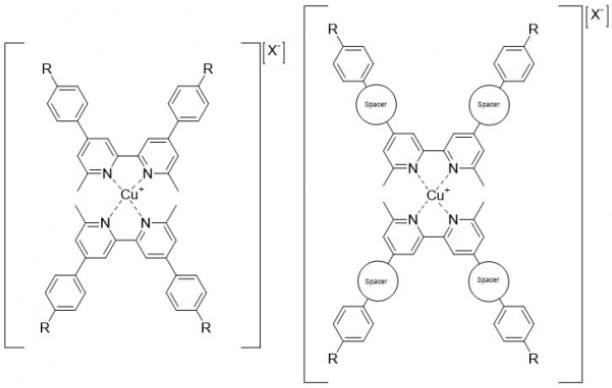


Figure: Homoleptic Cu(I) complexes of 6,6’dimethyl-4,4’-disubstituted-2,2’-dipyridyl ligands, with and without spacer on 4,4’ positions.

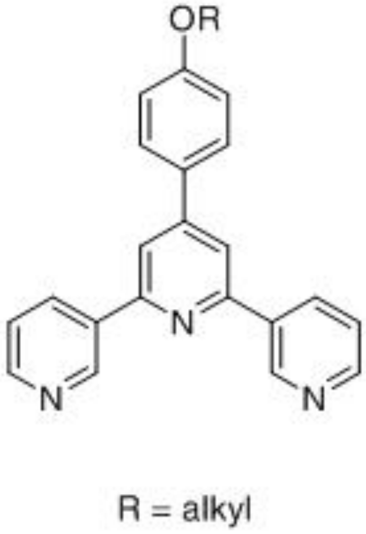
[1] B. O’Regan, M. Grätzel, Nature, **1991**, 353, 737-740;
[2] C. E. Housecroft and E. C. Constable, Chem. Soc. Rev., **2015**, 44, 8386.

# Ditopic 3,2':6',3''-terpyridine ligands: Diversity of coordination assemblies.

D. Rocco[1], A. Prescimone[1], C. E. Housecroft[1]*, E. C. Constable[1]*

[1]Department of Chemistry, University of Basel

New 3,2’:6’,3’’-terpyridine ligands (Scheme 1) have been prepared and characterized. Their coordination behavior towards metal salts including Co(NCS)$_2$ will be discussed and compared.



Scheme 1: ligand structure.

# A simple cerium-based fluorescent indicator displacement assay for the selective naked-eye detection of phosphate ions in water

T. Rossel[1], M. Creus[2], . Students GF Bienne[1]

[1]Pré Jean-Meunier 1, 2740 Moutier, [2]Klingelbergstrasse 50/70, 4056 Basel

A simple fluorescent indicator displacement assay (IDA) was used to probe phosphate ions into water by mixing only methylcalcein blue (MCB) and cerium ammonium nitrate (CAN). The fluorescence of MCB is quenched when added to CAN[1] in buffered conditions (HEPES 100 mM, pH = 7.4) and recovered by the addition of phosphate due to ligand exchange. Compared to previous results[2] presented in 2016, we show here that this simple homoleptic complex is able to detect selectively phosphate ions below micromolar concentrations, both spectrophotometrically and with the naked-eye. In addition, we will also present our efforts towards the detection of glyphosate.

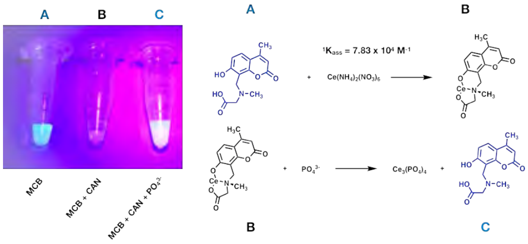


**Fig.1:** Mixing CAN (250 µM) with MCB (250 µM) **A** offers $[Ce(MCB)]^{2+}$ **B** (250 µM) a non-fluorescent water soluble inorganic complex. This inorganic complex **B** is exposed to the presence of anions. Upon exposition to sodium phosphate (250 µM), the complex **B** disassemble via an indicator displacement assay producing fluorescence visible with the naked-eye under the UV lamp at 254 and 400 nm.

[1] G. Britain, Analytical Chemistry., **1987**, 59, 1122-1125.
[2] T. Rossel, M. Creus, ChemRxiv, **2018.**

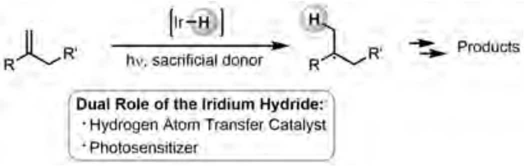
# Photoinduced Hydrogen Atom Transfer Reactions Catalyzed by Iridium Hydrides

M. R. Schreier[1], X. Guo[1], J. A. Kübler[1], O. S. Wenger[1]*

[1]University of Basel

The combination of photoredox catalysis and transition metal catalysis has gained broad attention as a method for novel chemical transformations.[1] Due to their capability to function both as strong photoacid[2] and as powerful hydride donor[3], iridium hydrides attracted particular interest as catalysts for diverse chemical reactions. Even though the reactivity of iridium hydrides has been thoroughly studied in recent years,[4] their capacity to transfer hydrogen atoms to non-activated olefinic substrates under irradiation with light seems to be unknown.

Our newly established system exploits the dual role of iridium hydrides to function both as photosensitizer and hydrogen atom transfer catalyst. Upon excitation of the iridium hydride with visible light, a hydrogen atom is transferred from the metal center to non-activated olefinic substrates. Depending on the reaction conditions, the formed radical intermediate can then undergo various consecutive radical reactions to form different products (Figure 1).



[1] C. K. Prier, D. A. Rankic, D. W. C. MacMillan, *Chem. Rev.*, **2013**, *113*, 5322-5363.
[2] T. Suenobu, D. M. Guldi, S. Ogo, S. Fukuzumi, *Angew. Chem. Int. Ed.*, **2003**, *42*, 5492-5495.
[3] S. M. Barrett, C. L. Pitman, A. G. Walden, A. J. M. Miller, *J. Am. Chem. Soc.*, **2014**, *136*, 14718-14721
[4] R. N. Perutz, B. Procacci, *Chem. Rev.*, **2016**, *116*, 8506-8544.

# Bioinspired Metal-Complexes as Chelators of Bacterial Metallo-β-Lactamase Zinc Ions

J. V. Schwarte[1], K. M. Fromm[1]*

[1]Fromm Group, Department of Chemistry, University of Fribourg

The bacterial metallo-β-lactamases are a current and pressing target for drug design. Indeed, they induce antibiotic resistance by participating in the hydrolysis of a whole class of antibiotics, the β-lactams (except monobactams), which are currently used worldwide.[1]

As illustrated below, their mechanism of action implies the participation of water molecules and zinc ions.

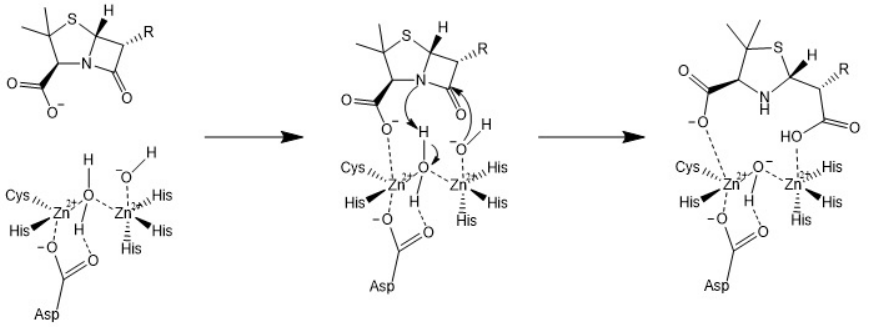


*Figure 1: Hydrolysis mechanism of β-lactam antibiotics inside the active site of metallo-β-lactamase, (inspired from* M-R. Meini, L. I. Llarrull, A. J. Vila, *FEBS Letters*/**2015,** 589, 3419–3432).

One possible way to inactivate these metallo-proteins could be the use of chelating drugs to remove the ions.[2] Therefore, the project aims at the extraction of the zinc ions from the active sites, and their replacement by a ligand or other metal ions. Expecting a synergetic effect, we are working on complexes between antibacterial metal-ion based compounds, and biocompatible and chelating molecules derived from amino acids.

[1] Yusralina Yusof, Daniel T. C. Tan, Omid Khalili Arjomandi, Gerhard Schenk, Ross P. McGeary, *Bioorganic Medicinal Chemistry Letters,* **2016**, 26, 1589-1593.

[2] Natasa Mitic, Manfredi Miraula, Christopher Selleck, Kieran S. Hadler, Elena Uribe, Marcelo M. Pedroso, Gerhard Schenk, *Advances in Protein Chemistry and Structural Biology,* **2014**, 97, 49-81.

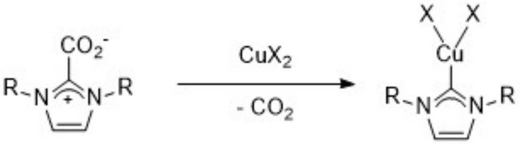
# Imidazolylidene copper(II) complexes: synthesis and re-arrangement behaviour

N. Ségaud[1], J. McMaster[2], G. van Koten[1,3], M. Albrecht[1]

[1]Departement für Chemie und Biochemie, Universität Bern, [2]School of Chemistry, University of Nottingham, Uni, [3]Utrecht University

Copper enzymes are efficient catalysts for electron transfer and dioxygen activation. Histidine is the common amino acid in the different active site types (Type 1, 2, 3 and CuA), and binds copper through a well-established N-bonding mode. In synthetic complexes, C-bonding to different metal centers has been observed by tautomerization processes. We are interested in inducing C-bonding rather than N-bonding of an imidazole and in investigating its effect on the activity of selected copper enzymes. For this purpose, N,N'-dimethylimidazolium-2-carboxylate (DMI-$CO_2$) has been used as an N-heterocyclic carbene (NHC) precursor. We successfully proved NHC-Cu(II) binding to a small protein Type 1 modified active site, where redox processes where facilitated by a C-bonding mode.[1]

Here we will present the synthesis and spectroscopic characterisation of a series of unprecedented copper(II) complexes with unsupported NHC ligands via a mild and general route and discuss specific factors that govern distinct re-arrangement patterns of these complexes.[2]



Financial support by the H2020 MSCA-IF, ERC and SNF is gratefully acknowledged.

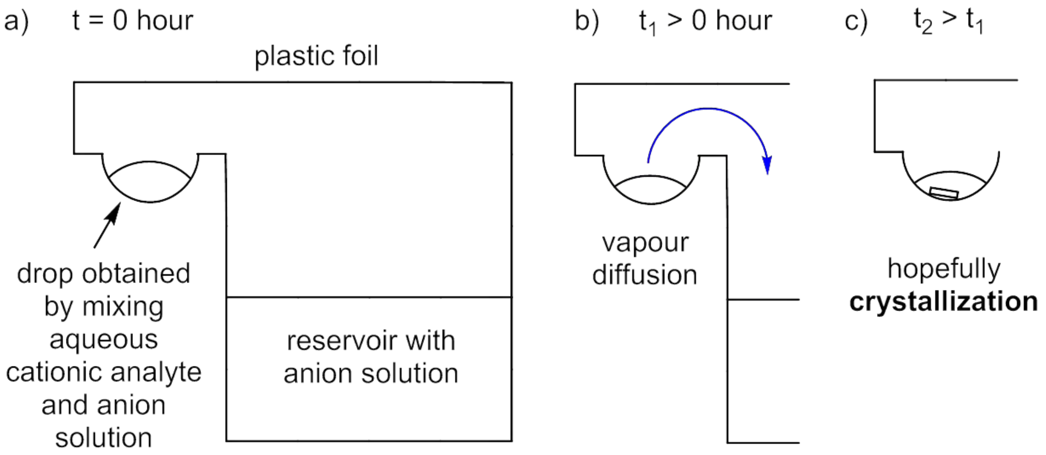
[1] Planchestainer, M.; Segaud, N.; Shanmugam, M.; McMaster, J.; Paradisi, F.; Albrecht, M. Carbene in Cupredoxin Protein Scaffolds: Replacement of a Histidine Ligand in the Active Site Substantially Alters Copper Redox Properties. *Angew. Chemie Int. Ed.* **2018**, 57, 10677–10682.
[2] Ségaud, N.; McMaster, J.; van Koten, G.; Albrecht, M. Manuscript in preparation.

# How to Crystallize Coordination Complexes, which are Stable in Water?

B. Spingler[1], R. Alvarez[1]

[1]University of Zurich

We have recently designed a crystallization screen consisting of 77 different anions and successfully applied the screen for the crystallization of six out of seven very diverse organic cations.[1, 2] The 96 different solutions of the screen are either mixed with the help of a pipetting robot[1] or just with a cheap multi-channel pipette under oil[2]. Vapour diffusion of water from the crystallization drops either in the bigger reservoir[1] (see Figure) or through the oil into the air[2] induces the growth of the crystals. In this presentation, we want to show our results of growing single crystals of various positively charged coordination compounds with the help of this crystallization screen.



[1] Philipp P. Nievergelt, Martin Babor, Jan Čejka, Bernhard Spingler, *Chem. Sci.*, **2018**, 9, 3716-3722.
[2] Martin Babor, Philipp P. Nievergelt, Jan Čejka, Vit Zvoníček, Bernhard Spingler, *IUCrJ*, **2019**, 6, 145-151.

# Solution-Phase Deposited Tin Sulfide (SnS) Thin Films For Water Splitting

J. Suh[1], D. Tilley[1]*

[1]Department of Chemistry, University of Zurich

SnS is a p-type semiconductor with a bandgap of 1.1-1.3 eV and large optical absorption coefficient in the visible. Its conduction band alignment is favorable for water reduction. Compared to CIGS (CuInGa(S,Se)) or CdTe, tin and sulfur are both earth abundant and non-toxic elements. Thus, SnS is a promising photocathode material for low-cost and large scale water splitting. Solution-phase deposition of inorganic semiconductor thin films is a facile and scalable method for manufacturing thin film photoelectrochemical (PEC) cells. In a binary solvent mixture of ethylenediamine and 1,2-ethanedithiol at 10:1 vol/vol ratio, bulk SnS powder dissolves and forms a molecular Sn-S ink [1]. Phase pure SnS thin films are then prepared by spin-coating the 0.5 M Sn-S ink on Au (100nm)-coated FTO (Fluorine doped Tin Oxide) and annealing in inert atmosphere at 350°C. Bare SnS shows very late onset potential for hydrogen reduction and is unstable in the acidic conditions of the PEC cell. To shift the onset voltage positively, different inorganic thin film buffer layers were grown by atomic layer deposition and chemical bath deposition to form a heterojunction. To improve the stability of the electrode, n-type $TiO_2$ (50 nm) was grown on top of the buffer layers. As a hydrogen evolution catalyst, Pt nanoparticles were deposited on the surface of $TiO_2$ by photoelectrodeposition. The champion photocathodes generate an onset voltage shift of +400 mV and a photocurrent density of -0.8 mA $cm^{-2}$ at 0 V versus reversible hydrogen electrode (RHE) for water splitting under 1 sun illumination. The photocurrent density does not decrease over time (30 min at 0 V vs RHE) showing that the SnS/buffer layer/$TiO_2$/Pt structure device has good stability for water splitting.

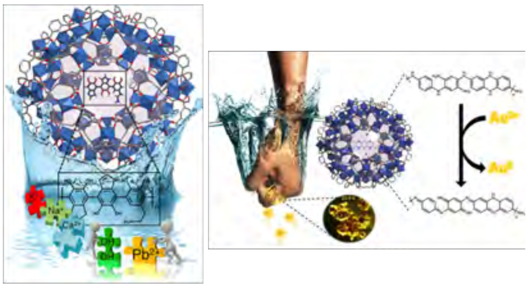
[1] Priscilla D. Antunez, Daniel A. Torelli, Fan Yang, Federico A. Rabuffetti, Nathan S. Lewis, and Richard L. Brutchey, *Chemistry of Materials,* **2014,** 26 (19), 5444-5446

# Design of Porous MOF/Polymer Composites for Selective and Enhanced Chemical Separations in Aqueous Media

D. T. Sun[1], W. L. Queen[2]*

[1]Laboratory for Functional Inorganic Materials, EPFL Lausanne, [2]Institut des Sciences et Ingénierie Chimiques, EPFL Lausanne

The discharge of toxic contaminants or commodities such as heavy and precious metals into the environment are of great concern. With the ever-increasing production of electronics, there is an ensuing need for gold extraction from sources other than virgin mines. As such, many strategies are under intense investigation for the extraction of such chemical species from their relevant mixtures. Recently we have developed a methodology to introduce extrinsic porosity to intrinsically non-porous polymers using MOFs as a template [1, 2]. Here we illustrate how we take advantage of unsaturated open metal sites inside of MOFs to facilitate the *in-situ* polymerization adhering the polymer to the pore surface. The result is a number of new porous composites with significantly enhanced properties for chemical separations in aqueous media. One composite, Fe-BTC/PpPDA, is shown to rapidly and selectively extract trace amounts of gold from several complex water mixtures that include wastewater, fresh water, ocean water, and solutions used to leach gold from electronic waste and sewage sludge ash [2]. The material has an exceptional removal capacity, 934 mg gold per gram of composite and also extracts gold from these complex mixtures at record-breaking rates, in as little as 2 min. Further, due to the high cyclability, we demonstrate that the composite can effectively concentrate gold and yield purities of 23.9 K, which is the highest purity of gold reported to date for these types of extraction processes. Designing novel MOF/Polymer composites for selective metal remediation from water with high energetic efficiency is of great importance and offers a significant challenge from a materials design perspective. In this work, the blueprint to synthesize MOF/Polymer composites that exhibit interesting host-guest properties for environmental contaminant and commodity remediation will be shown.



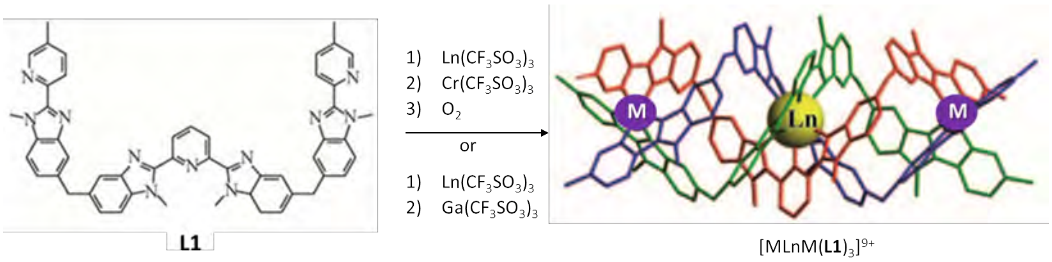
[1] D. T. Sun, L. Peng, W. S. Reeder, S. M. Moosavi, D. Tiana, D. K. Britt, E. Oveisi, W. L. Queen, *ACS Cent. Sci*, **4 (3)**, 349 – 356 (2018)
[2] D. T. Sun, N. Gasilova, S. Yang, E. Oveisi, W. L. Queen, J. *Am. Chem. Soc.*, **140 (48)**, 16697-16703 (2018)

# Self-Assembly of d–f heteronuclear triple helices

I. Taarit[1], S. Guerra[1], B. Doistau[1]*, C. Piguet[1]*

[1]Dept. of Inorganic and Analytical Chemistry, University of Geneva

The formation of supramolecular polymetallic edifices by self-assembly raised the chemist interest, but the synthesis of well-defined heterometallic architecture remain a challenge.[1] The mixture of labile metallic centres with designed polytopic ligand strands, using an accurate stoichiometry, is known as an efficient strategy to afford polymetallic helicates by self-assembly under thermodynamic control. The latter method was applied to segmental ligands[2] and permitted the formation of mixte d–f triple helicates allowing the observation of downshifting[3] and up-conversion phenomena implemented in molecular compounds.[4,5] We decided to further extend the well-defined Cr-Ln-Cr or Ga-Ln-Ga architectures to different lanthanides in order to explore the versatility of the up-conversion phenomenon or more generally energy conversion. The ligand synthesis will be presented as well as M-Ln-M triple helices self-assembly and photophysical experiments.



**L1**

$[MLnM(\mathbf{L1})_3]^{9+}$

[1] El Aroussi, B.; Zebret, S.; Besnard, C.; Perrottet. P. P.; Hamacek, J. *J. Am. Chem. Soc*. **2011**, *133*, 10764-10767.
[2] Piguet, C.; Bocquet, B.; Hopfgartner, G. *Helvetica. Chimica. Acta.* **1994**, *77*, 931-942.
[3] Aboshyan-Sorgho, L.; Nozary, H.; Aebischer, A.; Bünzli, J.-C. G.; Morgantini, P.-Y.; Kittilstved, K. R.; Hauser, A.; Eliseeva, S. V.; Petoud, S.; Piguet, C. *J. Am. Chem. Soc.* **2012**, *134*, 12675.
[4] Aboshyan-Sorgho, L.; Besnard, C.; Pattison, P.; Kittilstved, K. R.; Aebisher, A.; Bünzli, J. C. G.; Hauser, A.; Piguet, C. *Angew. Chem. Int. Ed.* **2011**, *50*, 4108-4112.
[5] Suffren, Y.; Zare, D.; Eliseeva, S. V.; Guénée, L. ; Nozary, H. ; Lathion, T. ; Aboshyan-Sorgho, L.; Petoud. S.; Piguet, C. *J. Phys. Chem. C.* **2013**, *117*, 26957-26963.

# Cooperativity in Spin Crossover Systems. An Atomistic Perspective on the Devils Staircase

S. Vela[1,3], H. Paulsen[2]

[1]Institute of Chemical Sciences and Engineering, École Polytechnique Fédérale de Lausanne (EPFL), Laboratory for Computational Molecular Design, CH-1015 Lausanne, Switzerland, [2]Institut für Physik, Universität zu Lübeck, Ratzeburger Allee 160, 23562 Lübeck, Germany, [3]Laboratoire de Chimie Quantique, Université de Strasbourg, 4 rue Blaise Pascal, Strasbourg, France

Spin Crossover (SCO) compounds are molecular materials that can be stable in two electronic states with different magnetic response, and whose relative stability can be interconverted by the application of external stimuli such as light, heat or pressure, among others. This quality makes them ideal candidates to be exploited in new electronic and spintronic devices, especially if the system features sufficient *cooperativity* to open an hysteresis loop.[1]

In this communication we present a study on the cooperativity of two solvatomorphs of the complex $[Fe^{II}(2\text{-pic})_3]Cl_2$ (**1**). This material displays a thermal SCO from a low-spin (LS) to a high-spin (HS) state with either gradual or abrupt character.[2] Extensive DFT computations (GGA+U+D2 level[3]) have been carried out to retrieve the energetics of successive steps of the LS-HS transition (Devil’s staircase), and rationalized using an extended Slichter-Drickamer model. The distinct shape of the spin transition displayed by the two solvatomorphs could be successfully reproduced and understood using the minimal experimental input (X-ray data). The microscopic origin of cooperativity is traced back to geometrical distortions of the $Fe\text{-}N_6$ core in case of the solvatomorph exhibiting an abrupt transition, with different contributions from the HS and LS molecules. This manifests in larger cooperativity values in the early steps of the LS-to-HS transformation. A computational protocol to discriminate the shape of a SCO transition without *a priori* assumptions is, thus, presented and validated for the case study.[4]

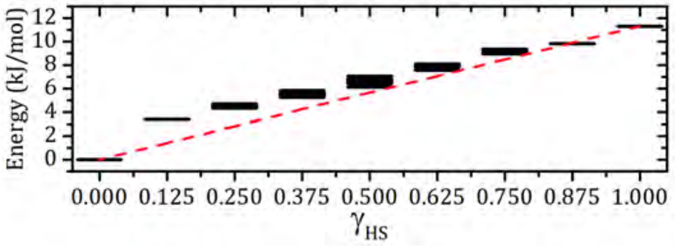


**Figure.** DFT energy energies (horizontal bars) of the 46 symmetry-unique magnetic configurations of the ethanol solvatomorph of **1** as a function of the HS fraction. Cooperativity is proportional to the difference between these energy levels and the non-cooperative energy (dashed line).

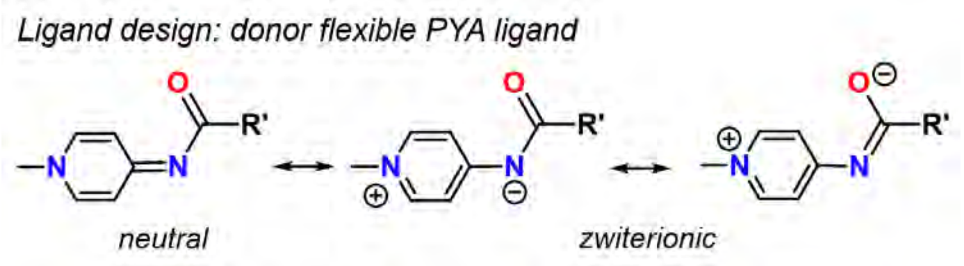
[1] Malcolm A. Halcrow, *Spin-Crossover Materials: Properties and Applications*, Wiley, Oxford, UK, **2013**.
[2] Marc Hostettler, Karl W. Törnroos, Dmitry Chernyshov, Brita Vangdal, Hans-Beat Bürgi, *Angew. Chem. Int. Ed.* **2004**, 43, 4589.
[3] Sergi Vela, Maria Fumanal, Jordi Ribas-Arino, Vincent Robert, *Phys. Chem. Chem. Phys.* **2015**, 17, 16306-16314
[4] Sergi Vela, Hauke Paulsen, *Inorganic Chemistry* **2018**, 57, 9478-9488.

# Base Metal Complexes of Chelating Pyridylidene Amide (PYA) Ligands for Oxidation Catalysis

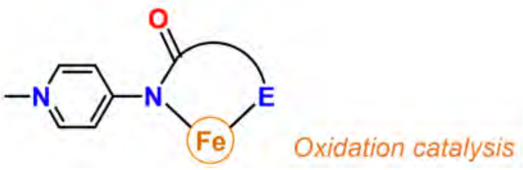
D. Verhoeven[1], M. Albrecht[1]*

[1]Departement für Chemie und Biochemie, Universität Bern

Ligands with flexible electron donating properties are of key interest in the development of first-row transition metal catalysts, as a means to overcome common one-electron reactivity by making use of metal-ligand cooperativity.[1] Examples of promising ligands are the pyridylidene-amide (PYA) ligands as a result of their unique electronic flexibility.[2] These ligands consist of an amide substituted with a methylated pyridine, which enables the presence of a) a neutral diene form, and b) a charge separated zwitterionic resonance structure, enhancing the electronic flexibility in the ligand and facilitating electron storage during a catalytic cycle (Figure 1).



In this research, the use of PYA ligands in combination with Earth-abundant iron is explored, merging the promising electronic features of this strongly donating ligand with an environmentally benign metal center. Chelating PYA ligands are employed to ensure strong and reliable coordination to iron (Figure 2). We will discuss synthetic aspects of these unprecedented PYA iron complexes and highlight their application as efficient catalysts in oxidation reactions.



[1] D.G.A. Verhoeven, M.-E. Moret, *Dalton Trans.*, **2016**, *45*, 15762–15778; J. R. Kusnutdinova, D. Milstein, *Angew. Chem. Int. Ed.*, **2015**, *54*, 12236–12273.

[2] K.F. Donnelly, C. Segarra, L.-X. Shao, R. Suen, H. Müller-Bunz, M. Albrecht,*Organometallics*, **2015**, *34*, 4076−4084; P. Melle, Y. Manoharan, M. Albrecht, Inorg. Chem., **2018**, *57*(18), 11761–11774; M. Navarro, C.A. Smith, M. Li, S. Bernhard, M. Albrecht, *Chem. Eur. J.*, **2018**, *24*, 6386–6398. M. Navarro, V. Rosar, T. Montini, B. Milani, M. Albrecht, *Organometallics*, **2018**, 37(*20*), 3619–3630.

# Single-layer poly(triazine imide) nanosheets for gas sieving

L. F. Villalobos[1], K. V. Agrawal[1]*

[1]Laboratory of Advanced Separations (LAS), École Polytechnique Fédérale de Lausanne (EPFL)

Poly(triazine imide) or PTI,[1] one of the few truly crystalline graphitic carbon nitrides synthesized so far, is a highly promising material for energy storage and conversion, sensors, and energy-efficient two-dimensional membranes.[2] However, the full potential of PTI can only be harnessed by (i) developing a scalable solid-state chemistry for the layered PTI (ii) exfoliating PTI crystals into single-layer nanosheets and, (iii) developing self-assembly strategies to process such nanosheets into coatings or thin films with a controlled number of layers. In this talk, I will describe efforts in such directions to use PTI for energy-efficient membranes. PTI is an extremely stable material that can withstand acidic and basic environments,[3] as well as temperatures of up to 600 °C. [4] This opens up the possibility of using PTI films for $H^+$ and $OH^-$ transport in electrolytic cells, and to recover $H_2$ directly from the effluent of the steam reforming process without having to cool it down. First-principles simulations form our part show that exfoliated PTI is promising for $H_2/N_2$, $H_2/CH_4$, $CO_2/N_2$ and $CO_2/CH_4$ separations.

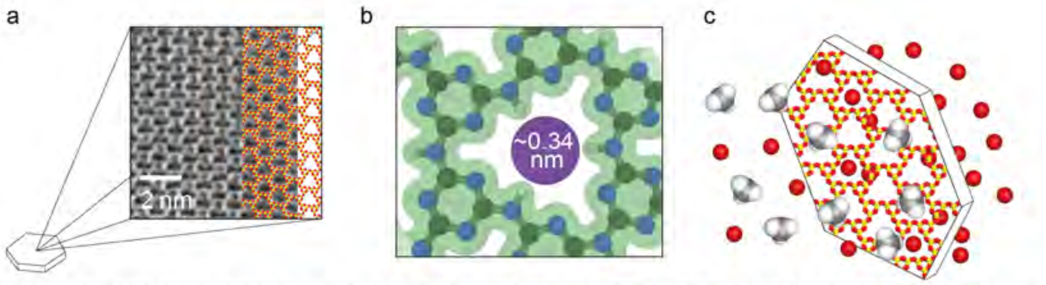


**Figure 1.** a) High-resolution transmission electron microscopy (HRTEM) image of a single-layer PTI nanosheet revealing the triangular pores. b) Electron density isosurface of a PTI pore showing the available space for molecules to transport. c) Diagram of a PTI nanosheet separating helium from methane molecules.

The scalable synthesis of highly crystalline PTI is challenging, because PTI requires a solid-state synthesis route using vacuum ampules.[1] Moreover, the exfoliation of PTI has been limited to few-layer nanosheets [4,5]. In fact, the triangular nanopores formed by imide-bridged triazine units in the individual layer of PTI have never been observed/imaged. Herein, we demonstrate a scalable ambient-pressure solid-state synthesis of PTI with 70% yield with respect to the precursor. We discuss a hot solvent-based exfoliation that leads to single-layer PTI, evidenced by the observation of the triangular nanopores of graphitic carbon nitride for the first time. Self-assembly of the exfoliated nanosheets yielded He and $H_2$ sieving membranes with $He/CH_4$ and $H_2/N_2$ selectivities of 98 and 93, respectively, making PTI nanosheets attractive for helium and hydrogen purification. Overall, we present the first demonstration of isolation and application of highly-crystalline nanosheets that are nanoporous and that are only an atom thick.

[1] E. Wirnhier, M. Döblinger, D. Gunzelmann, J. Senker, B. V. Lotsch, W. Schnick,*Chem. - A Eur. J.* **2011**, *17*, 3213.
[2] F. K. Kessler, Y. Zheng, D. Schwarz, C. Merschjann, W. Schnick, X. Wang, M. J. Bojdys, *Nat. Rev. Mater.* **2017**, *2*, 17030.
[3] K. Schwinghammer, B. Tuffy, M. B. Mesch, E. Wirnhier, C. Martineau, F. Taulelle, W. Schnick, J. Senker, B. V. Lotsch, *Angew. Chemie Int. Ed.* **2013**, *52*, 2435.
[4] T. S. Miller, T. M. Suter, A. M. Telford, L. Picco, O. D. Payton, F. Russell-Pavier, P. L. Cullen, A. Sella, M. S. P. Shaffer, J. Nelson, V. Tileli, P. F. McMillan, C. A. Howard, *Nano Lett.* **2017**, *17*, 5891.
[5] J. Jia, E. R. White, A. J. Clancy, N. Rubio, T. Suter, T. S. Miller, K. McColl, P. F. McMillan, V.

Brázdová, F. Corà, C. A. Howard, R. V. Law, C. Mattevi, M. S. P. Shaffer, *Angew. Chemie* **2018**, *130*, 12838.

# Structure-Property Relations in the $Ca_{1-x}Sr_xAlSi$ Solid Solution

D. I. Walicka[1], J. Lago[1,2], F. O. von Rohr[1]*

[1]Department of Chemistry, University of Zurich, CH-8057 Zurich, Switzerland, [2]Department of Inorganic Chemistry, Univ. del País Vasco, UVP/EHU, 48080, Bilbao, Spain

The discovery of the superconductivity in the layered compound $MgB_2$ with a critical temperature of $T_c$ = 39 K has sparked great interest in superconductors with related crystal structures. [1] Specifically CaAlSi and SrAlSi are ternary superconductors that crystallize in $AlB_2$-type structures with critical temperatures of $T_c$ = 8 K, and 5 K, respectively. [2] They surprisingly differ in properties among each other although they have similar electronic structures, and only a small difference in their crystallographic structures.

We have in a systematic approach analyzed the $Ca_{1-x}Sr_xAlSi$ solid solution and its evolution of the electronic and structural properties. We find that the superconductivity in this system is closely connected to the appearance of the structural distortion of the $[AlSi]_6^{2-}$ layers. Based on our results we establish the electronic phase diagram and compare it to the one of $MgB_2$.

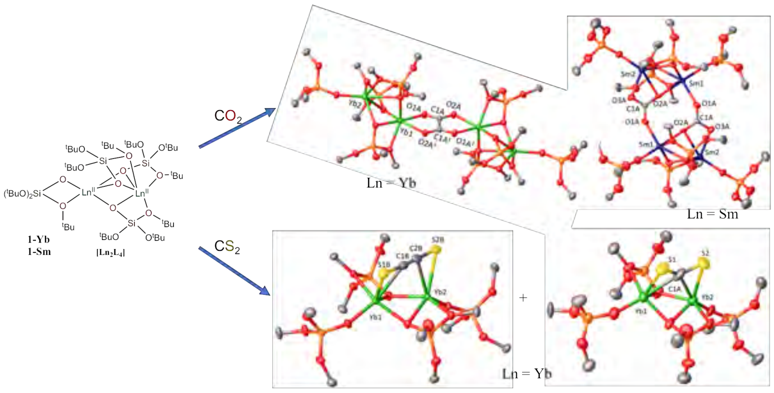
[1] Ma R., Huang G., Liu M., *Front. Phys. China*, **2007**, 2(2), 204—207.
[2] Lorenzet B., Cmaidalka J., Meng R. L., Chu C. W., *Phys. Rev. B*, **2003**, 68, 014512.

# Heteroallenes reduction by dinuclear Yb(II) and Sm(II) complexes supported by siloxide ligands.

A. R. Willauer[1], D. Toniolo[1], R. Scopelliti[1], F. Fadaei-Tirani[1], M. Mazzanti[1]*

[1]ISIC, Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland.

Small molecules activation by Ln(II) complexes has attracted increasing interest due to their redox properties and unique reaction pathways. In this purpose, the use of bulky, electron-rich tris(*tert*-butoxy)siloxide ligands are of interest to synthesize highly reactive divalent lanthanide complexes. Recently our group reported a rational route to mononuclear divalent "ate" complexes [Ln(OSi(O$^t$Bu)$_3$)$_4$K$_2$] (Ln = Eu, Yb, Sm) that have been shown to be potent reducing agents.[1] Small molecule activation by f-elements usually involves a multi-electron process and cooperative binding of the substrate has been shown to be important in order to promote their activation and reduction. Therefore, polymetallic complexes could be interesting targets, but small molecule reduction by polynuclear lanthanide complexes is scarce.



Here, we will report the synthesis of highly reactive dinuclear Ln(II) complexes [Ln$_2$(OSi(O$^t$Bu)$_3$)$_4$] (Ln = Yb, Sm) with unusually low coordination number. These complexes show interesting reactivity towards heteroallenes.[2,3] The reduction of CO$_2$ by the Yb(II) and Sm(II) complexes led to carbonate and oxalate where the selectivity of the reduction depends on the nature of the metal ion and the polarity of the solvent. Notably, crystals of the tetranuclear reduction products, [Yb$_4$L$_8$(C$_2$O$_4$)] and [Sm$_4$L$_8$(CO$_3$)$_2$], could be isolated from non-polar solvents, suggesting the interaction of two dinuclear complexes with carbon dioxide molecules in a non-polar solvent.[2] The reactivity of [Yb$_2$(OSi(O$^t$Bu)$_3$)$_4$] with CS$_2$ led to the first example of acetylenedithiolate formation from reduction of CS$_2$ by any metal complex, [Yb$_2$L$_4$(μ-C$_2$S$_2$)]. DFT calculation attributed this unique reactivity to the unusual binding mode of CS$_2^{2-}$ in the isolated intermediate product [Yb$_2$L$_4$(μ-CS$_2$)] which is resulting from the dinuclear nature of the Yb(II) complex.[3]

[1] J. Andrez, J. Pécaut, P.-A. Bayle, M. Mazzanti, *Angew. Chem. Int. Ed.* **2014**, *53*, 10448–10452.
[2] A. R. Willauer, D. Toniolo, F. Fadaei-Tirani, Y. Yang, M. Laurent, M. Mazzanti, *Dalton Trans.* **2019**, 48, 6100-6110.
[3] D. Toniolo, A. R. Willauer, R. Scopelliti, J. Andrez, Y. Yang, L. Maron, M. Mazzanti, *Chem. – Eur. J.* **2019**, DOI 10.1002/chem.201901321.

# Self-supported formation of Co-Fe-S box-like structure as a robust bifunctional electrocatalyst

Y. G. Zhao[1], G. R. Patzke[1]

[1]University of Zurich, Department of Chemistry

Low dimensional nanosized subunits (nanoparticles, nanosheets and nanorods), offer high surface area and active sites for efficient electrocatalyic water splitting while could largely reduce the ion transport pathways and promote electronic conductivity.[1] The three-dimensional microsized hollow structures, on the other hand, usually provided robust chemical stability, thus preventing the possible aggregation of active materials during the water reduction (hydrogen evolution reaction HER) or oxidation ( oxygen evolution reaction OER) process.[2] Therefore, the employment of complex micro/nano structures can address problems related to nano-unstablility or micro-low surface area for water splitting. The metal-organic framework (MOF) based materials offer several advantages, such as high design flexibility, tunable pore channels, large surface area, various metal centers and robust chemical stability. Rational design of MOF provides a great opportunity to construct highly efficient electrocatalysts for water splitting. Herein, we report a strategy to synthesize several Co-Fe-S based nanostructures (include nanocubes NCs, nanoboxs NBs and nanoparticles NPs) derived from PBA materials for the electrocatalytic oxygen evolution reactions OER. After sulfidation of the Co-Fe NBs, the Co-Fe-S NBs can be formed in self-templating approach, which show superior performance for OER.

[1] G. Q. Zhang and X. W. Lou, *Adv. Mater.*, 2013, 25, 976.
[2] C. Liu, F. Li, L. P. Ma, and H. M. Cheng, *Adv. Mater.*, 2010, 22, E28 E62.

CHIMIA

CHIMIA 2019, Volume 73
ISSN 0009-4293
www. chimia.ch
Supplementa to Issue 7-8/2019

SCS
Swiss Chemical
Society

## SCS Fall Meeting 2019
## Oral Presentation Abstracts

# Session of Inorganic & Coordination Chemistry

September 6, 2019
Irchel Campus, University of Zürich, Switzerland
http://scg.ch/fallmeeting/2019

Swiss Chemical Society
Haus der Akademien
Postfach
3001 Bern
Switzerland
info@scg.ch
www.scg.ch

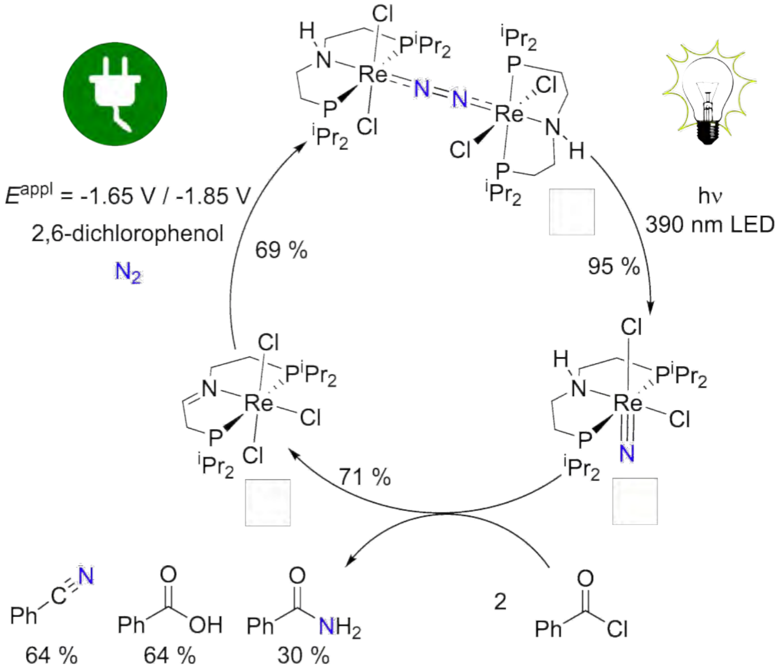
# Electrochemical and Photochemical Transformations of Dinitrogen

S. Schneider[1]

[1]Georg-August-Universität Göttingen, Tammannstr. 4, 37077 Göttingen, Germany
sven.schneider@chemie.uni-goettingen.de

The functionalization of dinitrogen to ammonia and particularly to organic nitrogen compounds, such as amines, nitriles or nitro compounds, at ambient conditions remains as one of the most challenging tasks in homogeneous catalysis. In turn, selective oxidations of ammonia or organic amines are of great importance, e.g. in the context of electrocatalytic ammonia combustion or nitrene transfer catalysis.

Our group examines elementary reactions relevant to $N_2$-fixation strategies, such as nitride hydrogenolysis and coupling, or $N_2$splitting into molecular nitrides and N-transfer from the resulting nitrides to organic molecules (Figure). In this context, mechanistic aspects of key reactions and electronic structure/reactivity relationships for pivotal intermediates will be discussed.



[1] I. Klopsch, M. Finger, C. Würtele, B. Milde, D. B. Werz, S. Schneider, *J. Am. Chem. Soc.* **2014**, *136*, 6881.
[2] I. Klopsch, M. Kinauer, M. Finger, C. Würtele, S. Schneider, *Angew. Chem. Int. Ed.* **2016**,*55*, 4786.
[3] G. A. Silantyev, M. Förster, B. Schluschaß, J. Abbenseth, C. Würtele, C. Volkmann, M. C. Holthausen, S. Schneider, *Angew. Chem. Int. Ed.* **2017**, *56*, 5872.
[4] B. M. Lindley, R. S. van Alten, M. Finger, F. Schendzielorz, C. Würtele, A. J. M. Miller, I. Siewert, S. Schneider, *J. Am. Chem. Soc.* **2018**, *140*, 7922.
[5] F. Schendzielorz, M. Finger, J. Abbenseth, C. Würtele, V. Krewald, S. Schneider, *Angew. Chem. Int. Ed.* **2019**, *58*, 830.

# Addressing Lattice Flexibility in Metal Organic Framework Membranes for Carbon Capture

D. J. Babu[1], K. V. Agrawal[1]*

[1]Laboratory of Advanced Separations (LAS), EPFL Lausanne

Metal-organic framework (MOF) membranes are advantageous to their nanoporous counterparts owing to a high degree of structural tunability, relatively fast crystallization kinetics, and higher reproducibility [1-3]. Although MOF membranes were first reported almost a decade ago, so far, an attractive $CO_2/CH_4$ or $CO_2/N_2$ separation performance has remained elusive. This is because MOFs possessing a pore aperture suitable for $CO_2$ sieving, typically suffer from lattice flexibility and gate-opening phenomena and as a result, a sharp molecular cut-off is not obtained. For example, ZIF-8, one of the most popular MOFs, has a crystallographically-determined pore aperture of 0.34 nm, ideal for separating $CO_2$ (kinetic diameter or k.d. of 0.33 nm) from $N_2$ (k.d. of 0.36 nm) and $CH_4$ (k.d. of 0.38 nm). However, $CO_2/CH_4$ or $CO_2/N_2$ selectivities greater than 5 have not been reported from the polycrystalline ZIF-8 membranes, hindering their application in biogas purification, natural gas sweetening and post-combustion carbon capture.

Here we report a novel post-synthetic rapid heat treatment (RHT) method, implemented in a few seconds between 320-400 °C, which drastically improves the carbon capture performance of the ZIF-8 membranes. Lattice stiffening is confirmed by the appearance of a temperature-activated transport, attributed to a stronger interaction of gas molecules with the pore aperture. Spectroscopic and X-ray diffraction studies confirm that while the coordination environment and crystallinity are unaffected, lattice distortion and strain are incorporated in the ZIF-8 lattice, increasing the lattice stiffness. Unprecedented $CO_2/CH_4$, $CO_2/N_2$, and $H_2/CH_4$ selectivities of up to 34, 37, and 200 respectively, which is an order of magnitude higher than the values reported so far for ZIFs, and a complete blockage of $C_3H_6$ is achieved [4]. Overall, the RHT treatment is a facile and versatile technique that can vastly improve the gas separation performance of the MOF membranes.

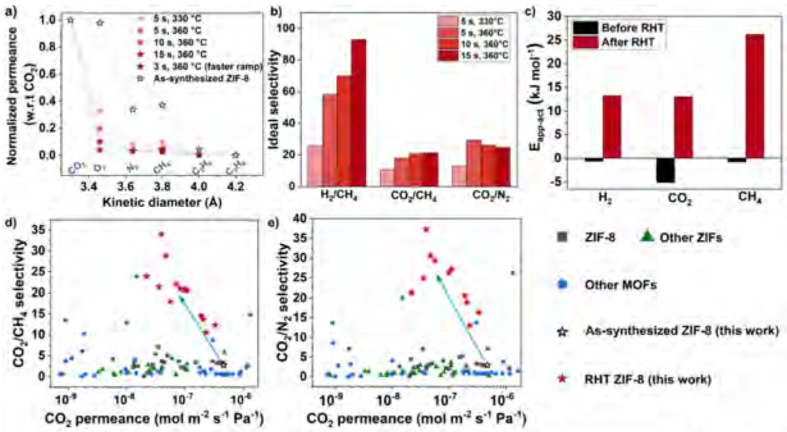


Figure 1: Gas separation properties of RHT ZIF-8 membranes: a) gas separation characteristics of ZIF-8 at 30°C as a function of RHT parameters. b) Ideal selectivities for various gas pairs at 30°C as a function of the dwell time and temperature. c) The calculated apparent activation energy for ZIF-8 membrane before and after RHT. Comparison of the $CO_2$ separation performance of RHT ZIF-8 membranes with other reported MOF membranes: d) $CO_2/CH_4$ and e) $CO_2/N_2$.

[1] Zhao, X.; Wang, Y.; Li, D. S.; Bu, X.; Feng, P. *Mater.* **2018**, *30* (37), 1705189.
[2] He, G.; Dakhchoune, M.; Zhao, J.; Huang, S.; Agrawal, K. V. *Funct. Mater.* **2018**, *28* (20), 1707427.
[3] Babu, D. J.; He, G.; Villalobos, L. F.; Agrawal, K. V. *ACS Sustain. Chem. Eng.* **2019**, *7* (1), 49–69.
[4] Babu, D. J.; He, G.; Hao, J.; Vahdat, M. T.; Schouwink, P. A.; Mensi, M.; Agrawal, K. V. *Advanced Materials*, **2019,** Just Accepted. doi:10.1002/adma.201900855.

# 100-fold Increase in Colloidal Stability of Cesium Lead Halide Perovskite Nanocrystals using Lecithin as Capping Ligand

F. Krieg[1,2], M. V. Kovalenko[1,2]*

[1]Institute of Inorganic Chemistry, Department of Chemistry and Applied Biosciences, ETH Zürich, [2] Laboratory for Thin Films and Photovoltaics, Empa – Swiss Federal Laboratories for Materials Science and Technology

Cesium and formamidinium lead bromide perovskite nanocrystals hold great promise for applications as down-converting green phosphors in liquid-crystal displays. In particular, they are unmatched and likely the only kind of emitter for so-called color-filter-free, front-pixel displays [1, 2]. Such pixels must exhibit near complete absorption of the blue backlighting and convert the blue excitation into green photoluminescence with near unity quantum efficiency. Towards these goals, perovskite NCs exhibit a five-fold higher absorption coefficient than their major contenders (InP-based quantum dots). Making such thick films through one-step solution processing, such as ink-jet printing or spin-coating, requires highly concentrated, aggregate-free nanocrystal inks. Using insights from the polymer physics on polymer brushes and our earlier experience with tightly binding zwitterionic capping ligands for perovskite NCs [3], we have identified lecithin as a ligand that is particularly suited for obtaining purified colloids with concentrations as high as 440 mg of NCs per one mL of solvent [4]. This enables the formation of micron-thick, optically smooth and optically clear films through one spin-coating step. At the same time these colloids can be diluted by 8 orders of magnitude, *ie*. down to 4 ng/mL, without compromising the colloidal and structural integrity of the NCs.

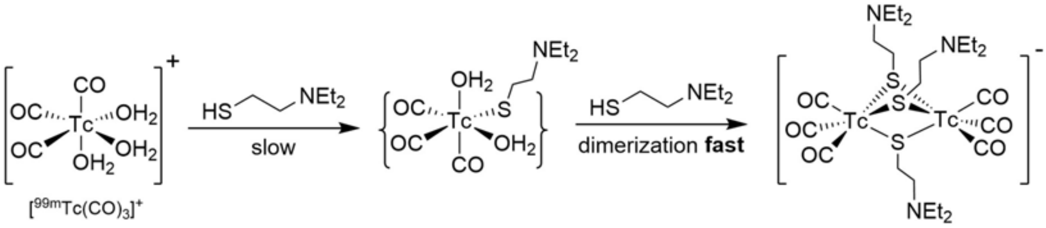
[1] Maksym V. Kovalenko and Maryna I. Bodnarchuk, *Chimia,* **2017**. 71, 461-470.
[2] Haiwei Chen, Juan He, and Shin-Tson Wu, *IEEE Journal of Selected Topics in Quantum Electronics*, **2017**. 23, 1-11
[3] Franziska Krieg, Stefan T. Ochsenbein, Sergii Yakunin, Stephanie ten Brinck, Philipp Aellen, Adrian Süess, Baptiste Clerc, Dominic Guggisberg, Olga Nazarenko, Yevhen Shynkarenko, Sudhir Kumar, Chih-Jen Shih, Ivan Infante and Maksym V. Kovalenko, *ACS Energy Letters,* **2018**, 3, 641-646.
[4] Franziska Krieg *et al*. submitted

# Chemistry at High Dilution: Dinuclear $^{99m}$Tc complexes do exist!

R. Bolliger[1], H. Braband[1], G. Meola[1], R. Alberto[1]*

[1]University of Zurich, Department of Chemistry, Winterthurerstrasse 190, 8057 Zürich

One of the most widely used radionuclides in nuclear medicinal diagnostics is $^{99m}$Tc (half-life time $t_{1/2}$ = 6h), the metastable form of the $^{99}$Tc-isotope ($t_{1/2}$ = 221ky). Its nearly ideal decay properties, such as half life time and decay energy of 140 keV, makes $^{99m}$Tc perfectly suited for Single Photon Emission Computed Tomography (SPECT).[1] All $^{99m}$Tc applications start with $[^{99m}TcO_4]^-$ from the elution of a $^{99}$Mo/$^{99m}$Tc generator with saline. The $^{99m}$Tc-concentrations are very small ($10^{-7}$ – $10^{-9}$ M) and thus the formation of di- or polynuclear complexes is kinetically unfavoured and there has not been a single report about the formation of a dinuclear $^{99m}$Tc-complex.[2] All reported $^{99m}$Tc-compounds are mononuclear, despite numerous reports of polynuclear $^{99}$Tc-compounds.[3,4] Different reaction conditions on the tracer ($^{99m}$Tc) and on the macroscopic level ($^{99}$Tc) might be responsible. Ligand concentrations are usually in $10^3$ – $10^6$ fold excess over $^{99m}$Tc, while equimolar concentrations with $^{99}$Tc apply. As there was no report of a di- or polynuclear $^{99m}$Tc complex, such complexes are believed to be synthetically inaccessible.



However, using appropriate bridging ligands (herein thiols HS-R) and a suitable $^{99m}$Tc-precursor $[^{99m}Tc(CO)_3(H_2O)_3]^+$, we demonstrate that dinuclear $^{99m}$Tc-complexes are formed at room temperature and at nanomolar concentrations. The dinuclear nature of $[^{99m}Tc_2(\mu_2\text{-}SR)_3(CO)_6]^-$ was assessed by chromatographic comparison with its rhenium homologue and with its true $^{99}$Tc analogue. Kinetic studies showed that the rate limiting step is not the dimerization, but the formation of a mononuclear $^{99m}$Tc-thiol complex, which rapidly dimerizes.[5]

[1] Shuang Liu, *Chem. Soc. Rev.,* **2004**, 33, 445-461.
[2] Roger Alberto, Henrik Braband, in: "Comprehensive Inorganic Chemistry II" J. Reedijk, K. Poppelmeier (ed.), **2013**, Elsevier, Oxford, 785-817.
[3] Henrik Braband, Ulrich Abram, *J. Organomet. Chem.*, **2004**, 689, 2066-2072.
[4] Francesco Tisato, Cristina Bolzati, Adriano Duatti, Giuliano Bandoli, Fiorenzo Refosco, *Inorg. Chem.* **1993**, 32, 2042-2048.
[5] Robin Bolliger, Angelo Frei, Henrik Braband, Giuseppe Meola, Bernhard Spingler, Roger Alberto, *Chem. Eur. J.*, 10.1002/chem.201901161.

# Bimetallic Dirhodium Complexes as Models to Study Hydrogen Activation on Carbon-Supported Rh(0) Catalysts

P. Jurt[1], T. L. Gianetti[2], A. Fedorov[1], H. Grützmacher[1]*

[1]D-CHAB, ETH Zürich, [2]Universtity of Arizona, Tucson

Supported rhodium catalysts are known as one of the most active catalysts for hydrogenation and dehydrogenation reactions.[1] However, the mode of interaction between Rh sites and $H_2$ is still not fully understood.[2] To gain further insight, we developed a series of bimetallic complexes bearing novel Rh(I) dimer moieties such as **1** and **3**. In comparison to heterogeneous catalysts, such model compounds allow for characterisation of the products by solution NMR techniques including parahydrogen induced polarization (PHIP) or $^{103}$Rh NMR. With dppm as ligand, complex **1** adds hydrogen reversibly in solution. Detailed DFT calculations allowed us to confirm that hydrogen activation precedes formation of **2** consistent with in situ NMR experiments (Figure 1, b). Remarkably, **1** activates $H_2$ in a very similar manner as was calculated for small rhodium clusters.[3] It is therefore a viable model compound for heterogeneous rhodium catalysts. Other complexes such as **3** transfer hydrogen to unsaturated C,C bonds in the ligand in a stepwise manner forming **4** and **5** (Figure 1, c). These reactions provide insight into conceivable pathways of hydrogen transfer to a carbon support which may be relevant for Rh/C hydrogenation catalysts.

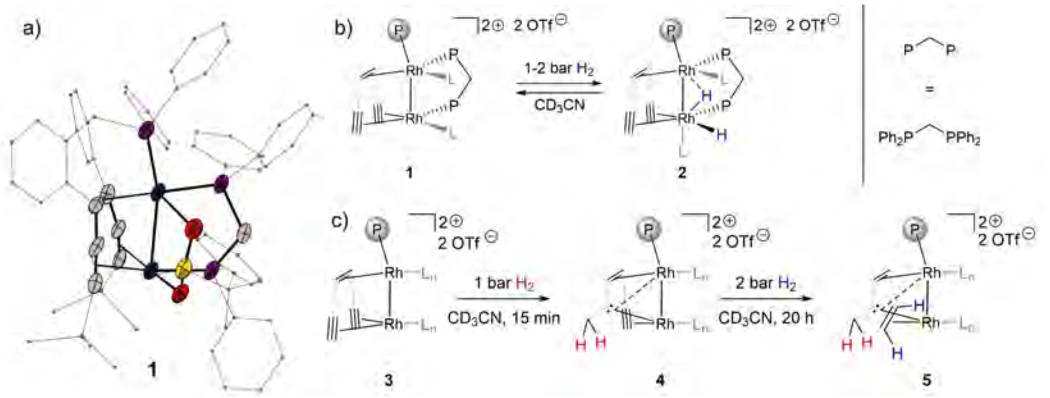


**Figure 1.** a) Crystal structure of **1**, b) hydrogen activation on **1** leads to dihydride species **2**, c) a stepwise $H_2$ addition to the rhodium-bound triple bonds in **3**. L is $CD_3CN$.

[1] Velina K. Markova, Georgi N. Vayssilov and Notker Rösch, *J. Phys. Chem. C*, **2015**, 119, 1121-1129.
[2] Pedro Serna and Bruce C. Gates, *Acc. Chem. Res.*, **2014**, 47, 2612-2620.
[3] Abhijit Dutta and Paritosh Mondal, *J. Phys. Chem. C*, **2018**, 122, 16925-16939.

# Quantitative insights into charge-separated states relevant for artificial photosynthesis

S. Neumann[1], C. Kerzig[1]*, O. S. Wenger[1]*

[1]University of Basel

Efficient multi-electron transfer reactions in photosynthesis rely on charge-separated states as key intermediates.[1] Despite the importance of charge-separated states, the factors that govern their formation efficiencies are still poorly understood.[2] Moreover, the desired charge accumulations compete with light-induced electron-hole recombinations as main deactivation pathways, which are largely unexplored.[3] Our study presents a systematic investigation[4] of two donor-photosensitizer-acceptor triads[5] capable of storing as much as 2.0 eV in their charge-separated states. Different donor-acceptor distances in the triads enabled us to include distance-dependence investigations. Using quantitative one-pulse laser flash photolysis, we provide deep insights into the charge-separated state formation quantum yields, which can reach up to 80%. Furthermore, the fate of the charge-separated state upon further (secondary) excitation with green photons is elucidated by additional two-pulse laser flash photolysis experiments[6]. One key finding of our study is that thermal and light-induced charge recombinations (Figure 1) show opposite behaviors in terms of their distance dependences.

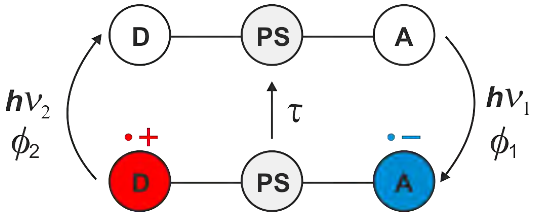


Figure 1: Schematic representation of the mechanism for light-induced ($h\nu_1$) formation of a charge-separated state in a molecular electron donor-photosensitizer-electron acceptor triad together with thermal ($\tau$) and light-induced ($h\nu_2$) charge recombination.

[1] Leif Hammarström, *Acc. Chem. Res.*, **2015**, 48, 840–850.
[2] Tomohiro Higashino, Tomoki Yamada, Masanori Yamamoto, Akihiro Furube, Nickolai V. Tkachenko, Taku Miura, Yasuhiro Kobori, Ryota Jono, Koichi Yamashita, Hiroshi Imahori, *Angew. Chem. Int. Ed.*, **2016**, 55, 629–633.
[3] Andrea Pannwitz, Oliver S. Wenger, *Chem. Commun.*, **2019**, 55, 4004–4014.
[4] Svenja Neumann, Christoph Kerzig, Oliver S. Wenger, *Chem. Sci.,* **2019**, DOI: 10.1039/c9sc01381d.
[5] Svenja Neumann, Oliver S. Wenger, *Inorg. Chem*., **2019**, 58, 855–860.
[6] Christoph Kerzig, Xingwei Guo, Oliver S. Wenger, *J. Am. Chem. Soc.*, **2019**, 141, 2122–2127.

# Enhanced charge carrier transport in sulfurized $Sb_2Se_3$ investigated by in-situ potential sensing and time-resolved spectroscopy

R. R. Prabhakar[1], T. Moehl[1], D. Fiedrich[2], W. Cui [1], D. Tilley[1]*

[1]University of Zurich, [2]Helmholtz Zentrum Berlin

$Sb_2Se_3$ has emerged as a promising photocathode for water splitting owing to its high photoelectrochemical performance (~ 15 $mAcm^{-2}$) and resistance to photocorrosion in the absence of any protection layers.[1] It has been demonstrated that sulfurization treatment of $Sb_2Se_3$ improves the onset potential and hence the photovoltage. However, the origin of such an improvement in the photovoltage is not fully understood in the literature. In this work, we employ 2 techniques to understand this phenomenon. Firstly, by employing a novel dual working electrode technique where the surface potential could be sensed and this was used to determine the photovoltage. By in-situ surface potential sensing, the photovoltage was found to increase from 220 mV to 340 mV upon sulfurization treatment. Next, from time-resolved microwave conductivity (TRMC), the carrier lifetimes and carrier mobilities were determined. Although the carrier mobilities remained the same, there was an increase in the carrier lifetime upon sulfurization treatment. Interestingly, this increase was more pronounced in shorter wavelengths (400-700 nm) than longer wavelength (700-1100nm) suggesting that the sulfurization treatment primarily reduces the surface recombination rather than bulk recombination. The carrier lifetimes obtained from $Sb_2Se_3$ were among the longest (in µs) in comparison to other emerging earth abundant materials like $BiVO_4$, $CuFeO_2$, $CuWO_4$ etc showing the immense potential of $Sb_2Se_3$ for photoelectrochemical water splitting applications.

[1] Rajiv Ramanujam Prabhakar, Wilman Septina, Sebastian Siol, Thomas Moehl, René Wick-Joliat and S. David Tilley *J.Mater. Chem. A*, **2017**,5, 23139-23145

# A new post-synthetic polymerization strategy makes metal-organic frameworks more stable

S. Yang[1], L. Peng[1], D. T. Sun[1], M. Asgari[1], E. Oveisi[2], O. Trukhina[1], S. Bulut[1], A. Jamali[1], W. L. Queen[1]*

[1]Institute of Chemical Sciences and Engineering, LFIM, École Polytechnique Fédérale de Lausanne (EPFL), [2]Centre for Electron Microscopy, EPFL, Lausanne

Metal-organic frameworks are of interest in a number of host-guest applications [1]. However, their weak coordination bonding often leads to instability in aqueous environments, particularly at extreme pH, and hence, is a challenging topic in the field [2]. In this work, a two-step, post-synthetic polymerization method is used to create a series of highly hydrophobic, stable MOF composites [3]. The MOFs are first coated with thin layers of polydopamine from free-base dopamine under a mild oxygen atmosphere, which then undergoes a Michael addition to covalently graft hydrophobic molecules to the external MOF surface (Fig. 1). This novel technique, which entails the use of free-base dopamine to graft hydrophobic HSF molecules onto the external MOF surface, significantly enhances MOF stability in water and in acidic or basic conditions. Free-base dopamine was selected as a binder between the MOF and HSF because it is a strong adhesive and polymerizes under a mild oxygen atmosphere at room temperature making it suitable to modify even the most unstable MOFs.

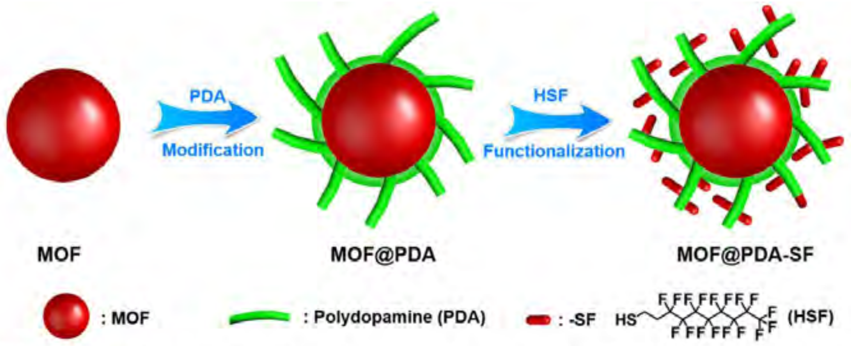


**Fig. 1** The modification process used to prepare hydrophobic MOF@PDA-SF composites.

This easy, mild post-synthetic could be applied to a number of composites using a structurally diverse set of MOFs with varying metals, ligands, and topologies. The as-prepared composites, including HKUST-1@PDA-SF, ZIF-67@PDA-SF, ZIF-8@PDA-SF, UiO-66@PDA-SF, Cu-TDPAT@PDA-SF, Mg-MOF-74@PDA-SF, and MIL-100-Fe@PDA-SF, show excellent stability even under harsh acid or basic conditions. Considering the novel results obtained from HKUST-1 and the many other structurally dissimilar frameworks, it is thought that this facile, mild method can be universally applied to improve the stability most MOFs and any other materials known to have water/pH instability. It is expected that this work can open doors to numerous new applications that were before inaccessible, and/or enhance MOF performance in existing areas coupled to catalysis, selective gas separation, delivery *etc.* by inhibiting decomposition, enhancing hydrophobicity and decreasing water permeability.

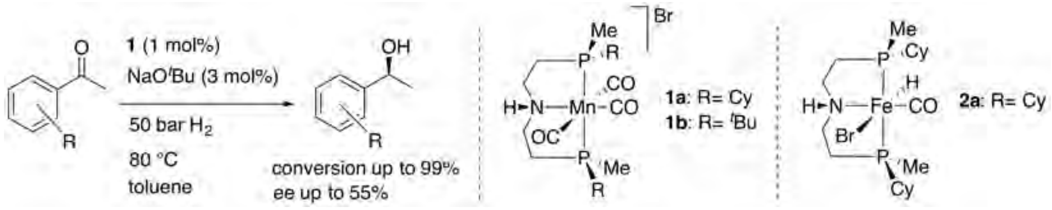
[1] a) H. Furukawa, K. E. Cordova, M. O'Keeffe, O. M. Yaghi, *Science*, **2013**, 341, 1230444; b) J. Lee, O. K. Farha, J. Roberts, K. A. Scheidt, S. T. Nguyen, J. T. Hupp, *Chem. Soc. Rev.*, **2009**, 38, 1450-1459.
[2] A. J. Howarth, Y. Liu, P. Li, Z. Li, T. C. Wang, J. T. Hupp, O. K. Farha, *Nat. Rev. Mater.,* **2016**, 1, 15018.
[3] S. Yang, L. Peng, D. Sun, M. Asgari, E. Oveisi, O. Trukhina, S. Bulut, A. Jamali, W. L. Queen, *Chem. Sci.*, **2019**, 10, 4542-4549.

# Manganese(I)-Catalyzed Asymmetric Hydrogenation of Ketones: Exploring the Analogy to Iron(II)

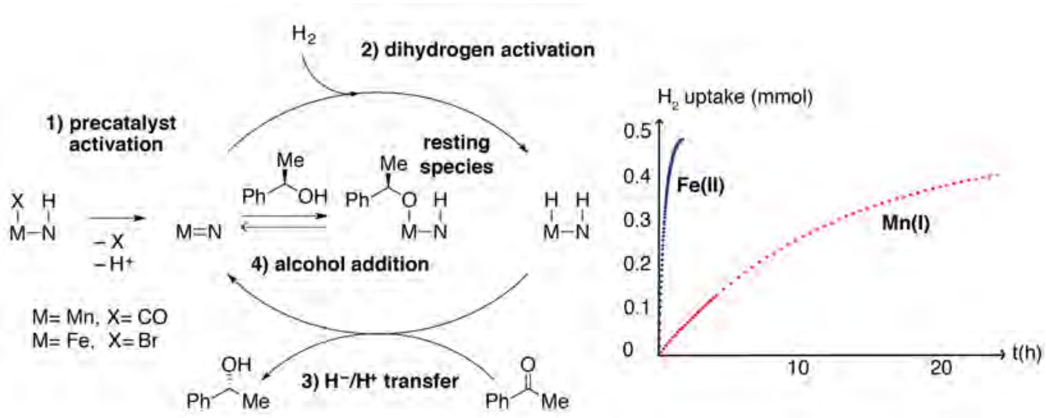
A. Passera[1], A. Mezzetti[1]*

[1]ETH Zürich

We describe here the first Mn(I) complexes with P-stereogenic PN(H)P pincer ligands (**1**) as catalysts for the asymmetric hydrogenation of ketones. Complex **1b** (1 mol%, 50 bar $H_2$, toluene, 80 °C) hydrogenates acetophenone to 1-phenylethanol with 99% yield and 55% ee after 16 h reaction time.



Furthermore, we studied **1a** for the sake of comparison with the iron(II) analogue **2a**, which has been previously prepared in our group.[1] The comparison between the isoelectronic manganese(I) and iron(II) hydrogenation catalysts has rapidly grown into a hot topic,[2] but no quantitative analysis has been reported to date. DFT calculations, NMR spectroscopic and kinetic studies indicate that the lower catalytic activity of Mn(I) is due to the large energetic span between the transition state of dihydrogen activation (**2**) and the alkoxide complex that is formed as resting species (**4**).[3]



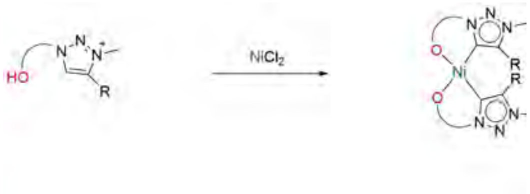
[1] R. Huber, A. Passera, E. Gubler, A. Mezzetti, *Adv. Synth. Catal.*, **2018**, *360*, 2900.
[2] a) G. A. Filonenko, R. van Putten, E. J. M. Hensen, E. A. Pidko, *Chem. Soc. Rev.*, **2018**, *47*, 1459; b) F. Kallmeier, R. Kempe, *Angew. Chem. Int. Ed.*, **2018**, *57*, 46; c) N. Gorgas, K. Kirchner, *Acc. Chem. Res.*, **2018**, *51*, 1558; d) L. Alig, M. Fritz, S. Schneider, *Chem. Rev.*, **2019**, *119*, 2681.
[3] L. de Luca, A. Passera, A. Mezzetti, *J. Am. Chem. Soc.*, **2019**, *141*, 2545.

# Nickel complexes containing oxygen-chelating mesoionic carbenes as easily accessible catalysts for $CO_2$ reduction

S. Bertini[1], M. Rahaman[1], F. Gloaguen[2], P. Schollhammer[2], P. Broekmann[1], M. Albrecht[1]*

[1]Departement für Chemie und Biochemie, Universität Bern, Switzerland., [2]UMR 6521, CNRS, Université de Bretagne Occidentale, CS 93837, 29238 Brest, France.

Research into new and efficient catalytic systems based on Earth-abundant metals represents a significant challenge for chemistry.[1] A key prerequisite to reach this goal is the availability of suitable ligands to stabilize the metal center. This field has been considerably stimulated by the discovery of N-heterocyclic carbenes (NHCs) as ligands that impart unique properties.[2] Triazolylidenes are a subclass of NHCs that are excellent σ-donors and have great electronic flexibility,[3] which allows for the stabilization of a wide variety of oxidation states of transition metals. Furthermore, their convenient synthetic modification provides access to heteroatom-functionalized NHCs for chelation.



Here we will present a facile and versatile synthesis of mesoionic ligands bearing a potentially chelating hydroxide moiety on the triazole scaffold as well as a new class of nickel(II) complexes containing these *C*,*O*-bidentate chelating mesoionic carbenes starting from a cheap and simple metal precursor. These nickel complexes show excellent activity and selectivity in $CO_2$ reduction, demonstrating great benefit of the hydroxyl group as chelating moiety for both the synthesis and the catalytic application of Earth-abundant metal complexes.

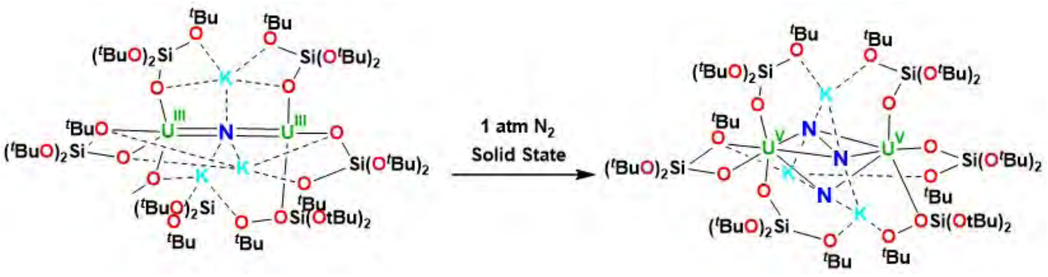
[1] R.M. Bullock, “Catalysis without precious metals”, **2011**, Wiley-VCH, Weinheim, Germany.
[2] K.H. Dötz, J. Stendel, *Chem. Rev.* **2009,** 109, 3227; F.E. Hahn, M.C. Jahnke, **2008**, 47, 3112; W.A Herrmann, *Angew. Chem. Int. Ed.*, **2002**, 41, 1290.
[3] J.D. Crowley, A. Lee, K. J. Kilpin, *Aust. J. Chem.*, **2011**, 64, 1118; K.F. Donnelly, A. Petronilho, M. Albrecht, *Chem. Commun.*, **2013**, *49*, 1145.

# Tuning Reactivity of Nitride Bridged Uranium Complexes with Amide and Siloxide Ligands

C. T. Palumbo[1], L. Barluzzi[1], R. Scopelliti[1], M. Mazzanti[1]*

[1]ISIC, École Polytechnique Fédérale de Lausanne (EP

Uranium nitride compounds have been implicated in dinitrogen fixation, N-atom transfer catalysis, and are proposed as advanced fuels in generation IV nuclear reactors. The chemistry of uranium nitride complexes is less developed than that of transition metals, but the highly polarizing nature of uranium, its large ionic radius, and *f* electrons that can interact with the ligands could allow new types of transformations. Recently, a bimetallic $U^{4+}$ nitride complex supported by the tris(tertbutoxy)siloxide ligand, $[Cs\{((Bu^tO)_3SiO)_3U\}_2(\mu\text{-}N)]$,[1] was reported and reacts with $CO_2$, CO, and $H_2$ to yield complexes of dicarbamate $(N(CO_2)_2)^{3-}$, cyanide $CN^-$, and an imide hydride complex, respectively; the $H_2$ reactivity is reversible.[2-4] Further, reduction of $[Cs\{((Bu^tO)_3SiO)_3U\}_2(\mu\text{-}N)]$ with excess $KC_8$ generated for the first time an isolable $U^{3+}$ nitride complex, $K_3[\{((^tBuO)_3SiO)_3\ U\}_2(\mu\text{-}N)]$,[5] which reduces $N_2$ to its tetraanion $(N_2)^{4-}$ to give a complex that facilitates subsequent functionalization.[6] The results to be presented describe attempts to prepare reactive uranium nitride complexes including those of $U^{3+}$ since $K_3[\{((^tBuO)_3SiO)_3U\}_2(\mu\text{-}N)]$ is the only known to date. Specifically, syntheses of complexes with amide ligands will be presented and comparisons between amide and siloxide ligands on small molecule and reduction reactivity will be made.



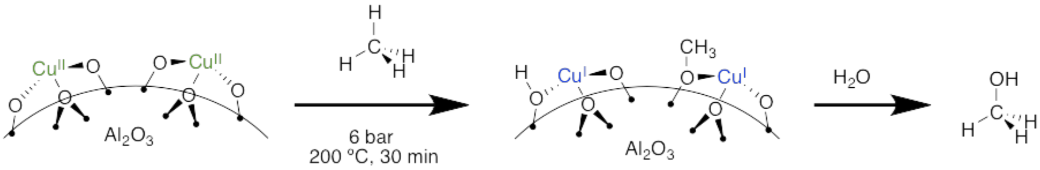
[1] Camp, C.; Pécaut, J.; Mazzanti, M. Tuning Uranium–Nitrogen Multiple Bond Formation with Ancillary Siloxide Ligands. *J. Am. Chem. Soc.* **2013**, 135, 12101–12111.
[2] Falcone, M.; Chatelain, L.; Mazzanti, M. Nucleophilic Reactivity of a Nitride-Bridged Diuranium(IV) Complex: $CO_2$ and $CS_2$ Functionalization. *Angew. Chem. Int. Ed.* **2016**, 55, 4074–4078.
[3] Falcone, M.; Kefalidis, C. E.; Scopelliti, R.; Maron, L.; Mazzanti, M. Facile CO Cleavage by a Multimetallic $CsU_2$ Nitride Complex. *Angew. Chem. Int. Ed.* **2016**, 55, 12290–12294.
[4] Falcone, M.; Poon, L. N.; Fadaei Tirani, F.; Mazzanti, M. Reversible Dihydrogen Activation and Hydride Transfer by a Uranium Nitride Complex. *Angew. Chem. Int. Ed.* **2018**, 57, 3697–3700.
[5] Chatelain, L.; Scopelliti, R.; Mazzanti, M. Synthesis and Structure of Nitride-Bridged Uranium(III) Complexes. *J. Am. Chem. Soc.* **2016**, 138, 1784–1787.
[6] Falcone, M.; Chatelain, L.; Scopelliti, R.; Zivkovic, I.; Mazzanti, M. Nitrogen Reduction and Functionalization by a Multimetallic Uranium Nitride Complex. *Nature* **2017**, 547, 332–335.

# Proximal Monomeric Cu(II) Sites on Alumina Convert Selectively $CH_4$ to $CH_3OH$

J. Meyet[1], K. Searles[1], M. Newton[1], A. P. van Bavel[2], A. D. Horton[2], J. A. van Bokhoven[1,3]*, C. Copéret[1]*

[1]Department of Chemistry and Applied Biosciences, ETH Zürich, [2]Shell Global Solutions International B.V., [3]Laboratory for Catalysis and Sustainable Chemistry, Paul Scherrer Institute

The conversion of methane to methanol is of significant economic and environmental importance, but this transformation remains a grand challenge due to the favored formation of over-oxidation products.[1] In contrast, methane monooxygenases, which are enzymes based on Cu or Fe metal centers, are very selective for this reaction and have thus been an inspiration for catalyst design. Of the various systems studied, Cu-exchange zeolites have shown the greatest potential for the selective oxidation of methane to methanol. Stepwise reaction conditions are employed to avoid the intrinsic low yield associated with direct catalytic oxidation.[2] However, despite years of research, the identity and nuclearity of the active site is still under debate.[3]
In that context, surface organometallic chemistry (SOMC)[4] combined with thermolytic molecular precursors (TMP)[5] has emerged as a powerful approach to generate isolated metal sites with controlled nuclearity and oxidation state on oxide supports for a broad range of metals. Herein, we show that this approach allows generating on non-porous alumina support Cu(II) sites that convert methane into methanol with high selectivity (> 80%). Through combined X-ray absorption (XAS) and electron paramagnetic resonance (EPR) spectroscopies, we show that this reaction takes place on pairs of monomeric Cu(II) sites in close proximity.[6] This discovery contrasts with the active centers proposed in Cu-exchanged zeolites, where $\mu^2$-$Cu_2O_2$ or $[Cu_3O_3]^{2+}$ are proposed, but parallels the most recent findings on particulate methane monooxygenases (pMMO) where the presence of only mononuclear Cu centers are proposed.[7]



*Scheme for the partial oxidation of methane to methanol*

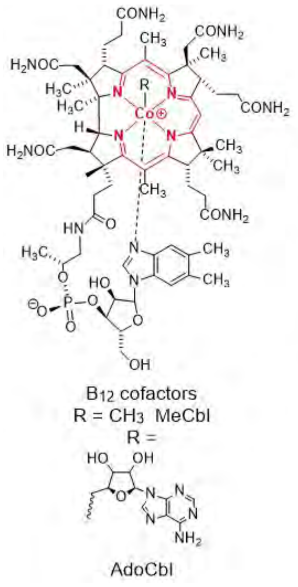
[1] a) Crabtree et al. *Chem. Rev.* **1995**, *95, 987-1007* b) Labinger et al. *Nature* **2002**, *417*, 507-514 c) Schwarz et al. *Angew. Chemie Int. Ed.* **2011**, *50*, 10096-10115 d) Ravi et al. *Angew. Chem. Int. Ed.* **2017**, *56*, 16464-16483
[2] a) Groothaert et al. *J. Am. Chem. Soc.* **2005**, *127*, 1394-1395 b) Alayon et al. *Chem. Commun.* **2012**, *48*, 404-406
[3] a) Woertink et al. *Proc. Natl. Acad. Sci.* **2009**, *106*, 18908-18913 b) Grundner et al. *Nat. Commun.* **2015**, *6*, 7546 c) Snyder et al. *Chem. Rev.* **2018**, *118*, 2718-2768 d) Sushkevich et al. *Angew. Chem. Int. Ed.*, **2018**, *57*, 8906-8910
[4] a) Copéret et al. *Angew. Chem. Int. Ed.* **2018**, *57*, 6398-6440 b) Copéret et al. *Acc. Chem. Res.* **2019** - under revision
[5]Fujdala et al. *Topics Organometal. Chem.* **2005**, *16*, 69–11
[6] Meyet et al. *Angew. Chem. Int. Ed.* **2019** – in press (doi: 10.1002/ange.201903802)
[7] Ross et al. *Science* **2019**, *364*, 6440

# A Novel Ni-containing $B_{12}$ Derivative – Elucidating the Origin of Corrinoid and Corphinoid Cofactors

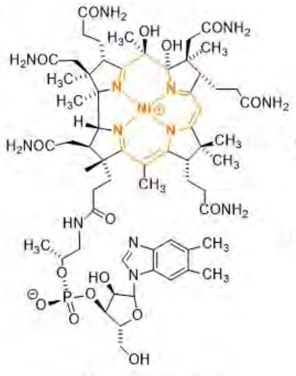
C. Brenig[1], L. Prieto[1], R. Oetterli[1], F. Zelder[1]*

[1]Department of Chemistry, University of Zurich, Winterthurerstrasse 190, 8057 Zurich, Switzerland

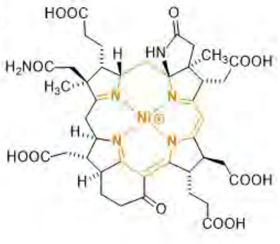
For a better understanding of biological processes catalyzed by transition metal complexes with porphinoid ligands, it is important to discern why different structural alterations of one ligand system were chosen by nature in order to accommodate a specific metal center. Some important porphinoid cofactors that display a high structural complexity are the $B_{12}$ cofactors methylcobalamin (MeCbl) and 5'-deoxyadenosylcobalamin (AdoCbl), as well as cofactor F430. While the two former cofactors, derived from vitamin $B_{12}$, play important roles in the metabolism of methionine and folate, nucleotide synthesis[1] and the breakdown of odd fatty acids,[2] the latter ("F430") is found only in methanogenic bacteria where it catalyzes the formation – as well as the oxidation – of methane.[3] Recently we accomplished the first partial chemical synthesis of a cobalamin derivative starting from vitamin $B_{12}$, that contains a central nickel ion instead of cobalt. Key step of the synthetic route was the simultaneous demetallation and ring closure of a ring-opened 5,6-*seco*-cobalamin. The resulting 'nibalamin' derivative shares spectroscopic features with F430 that are attributed to structural similarities of the tetradentate ligand framework.[4]



B12 cofactors
R = CH3 MeCbl
R =
AdoCbl



semi-synthetic
"nibalamin"



cofactor F430

The coordination chemistry of this hybrid F430–$B_{12}$ species, however, supports pioneering work of the Eschenmoser group regarding why nature has combined Ni with a corphin rather than a corrin ligand in F430 to allow for challenging biochemical transformations.[5] Semi-synthetic metallocorrins can shed new light on the old question of corrin vs. corphin ligand in nature but might as well bear potential for applications in analytical and medicinal science. Financial support by the Forschungskredit of the University of Zurich (grant FK-17-088) is gratefully acknowledged.

[1] R. Banerjee, S. W. Ragsdale, *Annu. Rev. Biochem.* **2003**, 72, 209–247. [2] R. Banerjee, *Chem Rev* **2003**, 103, 2083–2094. [3] A. Pfaltz, D. A. Livingston, B. Jaun, G. Diekert, R. K. Thauer and A. Eschenmoser, *Helv. Chim. Acta* **1985,** 68, 1338–1358. [4] C. Brenig, L. Prieto, R. Oetterli and F. Zelder, *Angew. Chem. Int. Ed.* **2018**, 57, 16308–16312. [5] A. Eschenmoser, *Angew. Chem. Int. Ed.* **2011**, 50, 12412–12472.