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Inorganic and Coordination Chemistry **IC01**

Supramolecular strategies in Transition metal catalysis

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The interface between supramolecular chemistry and transition metal catalysis has received surprisingly little attention in contrast to the individual disciplines. It provides, however, novel and elegant strategies that lead to new tools for the search of effective catalysts, 1 and as such this has been an important research theme in our laboratories. In this presentation I will focus on supramolecular strategies to control selectivty in transition metal catalysis, which is especially important for reactions that are impossible to control using traditional catalyst development. For substrates with functional groups we use substrate orientation effects to control selectivty, whereas for non-functionalized substrates we create cages around the active transition metal. Next to supramolecular control, supramolecular approaches appear ideally suited for the creation of large ligand libraries. The large number of catalyst that become available in this manner, asks for screening strategies and evolutionary approaches. A first academic example of catalyst selection from a mixture will be discussed. In addition, the application of a cofactor strategy will be presented, which is also ideally suited for selection procedures. In addition to the new concepts I will also show some examples in which we use these strategy in synthesis

References: a) JNH**,** Reek et al ***Org. Biol. Chem.,*** 3, **2005**, 2371; 1b) *Chem. Eur. J.*, **2006**, *12,* 4219; 1c) *J. Am. Chem. Soc.* **2006**, *128*, 11344; 1d) *Chem. Commun.* **2006** 4679. 1e) *Dalton. Trans* **2006,** 2308; 1f) *Angew. Chem. Int. Ed.* **2006**, *45*, 1223; 1g) *Angew. Chem. Int. Ed.* **2008**; 1h) *J. Am. Chem. Soc.* **2009** *131*, *Angew. Chem. Int. Ed.* **2009**; *Angew. Chem. Int. Ed.* **2011,** 7342; *Angew. Chem. Int. Ed.* **2011**, 396; *Nature Chemistry* **2010**, 615**;** *Nature Chemistry* **2010,** 417. 1f) *J. Am. Chem. Soc.* **2011**, 17176; *J. Am. Chem. Soc.* **2012.** 1260**.**

Inorganic and Coordination Chemistry **IC02**

Catalytic H_2 production from biomass-relevant alcohols under mild conditions

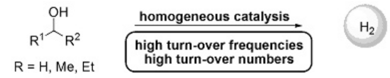
M. Nielsen, E. Alberico, A. Monney, H. Junge and M. Beller

Leibniz-Institut für Katalyse e.V (LIKAT Rostock), Albert-Einstein-Strasse 29A, 18059 Rostock, Germany

The quality of human life is mainly determined by the availability of material and energy resources. However, it is now clear that the use of coal, gas and oil is limited and a switch to renewable energy resources is therefore essential. Hydrogen has become a very promising option as alternative energy source since it can be converted efficiently into electrical energy *via* H_2/O_2 fuel cells, releasing only water as benign exhaust. In recent years, an increasing interest has emerged in the use of biomass or its fermentation products, *e.g.* alcohols, as promising feedstock for the generation of hydrogen.

Here we present our achievements in the acceptorless dehydrogenation of biomass-relevant alcohols under mild conditions [1].

In addition, the first example of aqueous-phase methanol reforming by homogeneous catalysis will be presented [2]. Our highly efficient and stable ruthenium catalysts produce hydrogen with TOF_{max} approaching 50000 h^{-1} and $TON_{max} > 350000$. These results would make the delivery of hydrogen on mobile devices–and hence the use of methanol as a practical hydrogen carrier–feasible.



[1] a) M. Nielsen, A. Kammer, D. Cozzula, H. Junge, S. Gladiali and M. Beller, *Angew. Chem. Int. Ed.* **2011**, *50*, 9593; b) M. Nielsen, H. Junge. A. Kammer and M. Beller, *Angew. Chem. Int. Ed.* **2012**, *51*, 5711.

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Inorganic and Coordination Chemistry **IC03**

Highly Monodisperse Tin Nanocrystals as Anode Material in High-Performance Lithium-ion batteries

Marc Walter, Kostiantyn Kravchyk, Loredana Protesescu, Maryna I. Bodnarchuk, Frank Krumreich, Maksym Yarema, Christoph Guntlin and Maksym V. Kovalenko

ETH Zurich, Wolfgang-Pauli-Str. 10, CH-8093 Zurich, Switzerland.

EMPA-Swiss Federal Laboratories for Materials Science and Technology, Überlandstrasse 129, CH-8060 Dübendorf, Switzerland.

Tin-based anode materials can substantially improve the performance of Lithium-ion batteries, notably their energy density and electrode capacity, since Tin can accommodate Li reversibly with a theoretical maximal capacity of 991 mAh/g (for $Li_{4.4}Sn$) [1]. However, upon insertion and extraction of Li Tin undergoes large volume changes (over 300%) causing pulverization of the electrode and consequently capacity fading after a few cycles. To overcome this issue, highly monodisperse Sn nanocrystals were synthesized under precise size control and tested as potential anode material [2]. The insulating organic ligands used for synthesis were exchanged by small inorganic ligands in order to improve the electronic connectivity within the components of the electrode material. Li-insertion properties of inorganically capped Sn/SnO_2 nanocrystals showed size-dependent character achieving up to three times higher gravimetric and volumetric energy densities than commercial graphite electrodes under close to practical electrochemical cycling conditions.

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Inorganic and Coordination Chemistry **IC04**

Trithiolato-bridged Dinuclear *p*-Cymene Ruthenium Complexes: A Study of their High *in vitro* Anticancer Activity

Federico Giannini[a], Julien Furrer[a] and Georg Süss-Fink[b]

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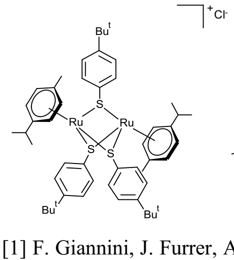
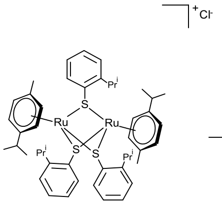
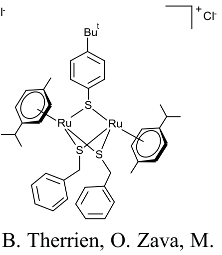
b. Institut de Chimie, Ave Bellevaux 51, CH-2000, Neuchâtel, Switzerland

We recently synthesized three series of thiophenolato-bridged dinuclear *p*-cymene ruthenium complexes of general formula $[(\eta^6\text{-}p\text{-}MeC_6H_4Pr^i)_2Ru_2(SR)_3]^+$, which proved to be highly cytotoxic against human ovarian cancer cells A2780 and their cisplatin resistant mutant A2780cisR, the IC_{50} values being in the nanomolar range.[1] We investigated by NMR the incubation with biological targets such as nucleotides and peptides and we found them to catalyze the oxidation of the cysteine-containing tripeptide glutathione (GSH) to its oxidized form (GSSG).[1] A correlation between the complex cytotoxicity, lipophilicity and the Hammett constants was possible.[1] Here, we present our results obtained, by NMR and CD spectroscopy, by incubation of some of these derivatives with four proteins implicated in relevant biological processes: albumin, transferrin, myoglobin and ubiquitin.







[1] F. Giannini, J. Furrer, A.F. Ibao, G. Süss-Fink, B. Therrien, O. Zava, M. Baquie, P.J. Dyson, P. Štěpnička, *J. Biol. Inorg. Chem.* **2012**, *17*, 951

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Inorganic and Coordination Chemistry

IC01

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Inorganic and Coordination Chemistry

IC02

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Leibniz-Institut für Katalyse e.V (LIKAT Rostock), Albert-Einstein-Strasse 29A, 18059 Rostock, Germany

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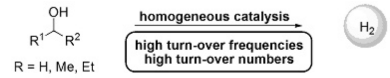

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Inorganic and Coordination Chemistry

IC03

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Inorganic and Coordination Chemistry

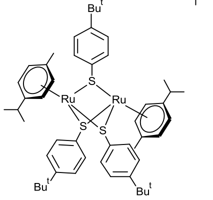
IC04

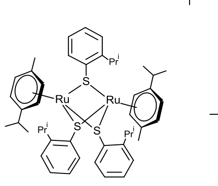
Trithiolato-bridged Dinuclear *p*-Cymene Ruthenium Complexes: A Study of their High *in vitro* Anticancer Activity

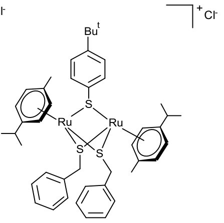
Federico Giannini[a], Julien Furrer[a] and Georg Süss-Fink[b]

a. Departement für Chemie und Biochemie, Freiestrasse 3, CH-3012, Bern, Switzerland
b. Institut de Chimie, Ave Bellevaux 51, CH-2000, Neuchâtel, Switzerland

We recently synthesized three series of thiophenolato-bridged dinuclear *p*-cymene ruthenium complexes of general formula $[(\eta^6\text{-}p\text{-}MeC_6H_4Pr^i)_2Ru_2(SR)_3]^+$, which proved to be highly cytotoxic against human ovarian cancer cells A2780 and their cisplatin resistant mutant A2780cisR, the IC_{50} values being in the nanomolar range.[1] We investigated by NMR the incubation with biological targets such as nucleotides and peptides and we found them to catalyze the oxidation of the cysteine-containing tripeptide glutathione (GSH) to its oxidized form (GSSG).[1] A correlation between the complex cytotoxicity, lipophilicity and the Hammett constants was possible.[1] Here, we present our results obtained, by NMR and CD spectroscopy, by incubation of some of these derivatives with four proteins implicated in relevant biological processes: albumin, transferrin, myoglobin and ubiquitin.







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Inorganic and Coordination Chemistry **IC05**

Reactivity of hexaruthenium assemblies towards nucleotides and DNA

Lydia Paul[1], Julien Furrer[1], Bruno Therrien[2]

[1]Departement of Chemistry and Biochemistry, University of Berne.
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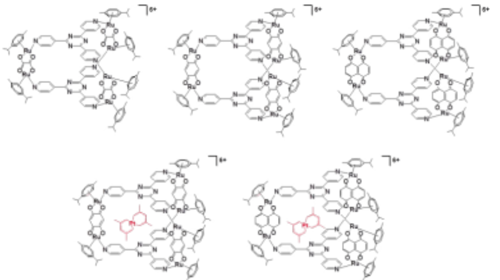
Over the last decades, ruthenium-based anticancer drugs have become the focus of research, since they are known to cause fewer side effects than platinum drugs [1-3]. In recent years, we have designed different hexacationic hexaruthenium assemblies that can encapsulate various guest molecules, which makes them useful for drug delivery to cancer cells [4]. Now, the aim of our work is to assess the behavior of the ruthenium assemblies under physiological conditions, with or without an encapsulated guest molecule, using various NMR techniques. It is important to determine if DNA is a likely target for the ruthenium assemblies, therefore we monitored the interaction between the assemblies both with isolated nucleotides and DNA strands.



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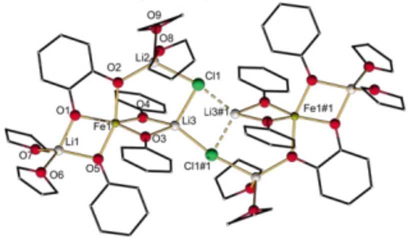
Inorganic and Coordination Chemistry **IC06**

New metal Aryloxide complexes as ceramic precursors and Initiators for Ring-Opening Polymerization

Yvens Chérémond, Katharina M. Fromm

University of Fribourg, CH-1700 Fribourg, Switzerland

In addition to the development of new energy-producing processes, finding new energy-saving procedures offers a promising solution to meet our energy needs in the long run. Indeed, cheap organometallic precursors for oxide materials and competitive catalyst are key technologies for energy saving. A wide variety of metal alkoxides/aryloxides[1] has been used not only as precursors for oxide materials, but also as initiators and catalysts for ring-opening polymerization (ROP). Ceramic oxide materials are widely used for many applications, exceptionally in lithium-ion batteries (LIB) material for the last recent decades. For the cited reasons, iron-based aryloxide complexes offer many advantages, such as the large abundance of iron, their low toxicity and even their biocompatibility[1].



For this purpose, the authors will present new and cheap heterometallic iron based aryloxide complex[2] as an initiator for ring-opening polymerization(ROP) of lactide and also precursors for ceramic oxide materials.

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Inorganic and Coordination Chemistry **IC07**

^{119}Sn Surface Enhanced NMR Spectroscopy as a Tool to Probe Silica Surface Heterogeneity

Aleix Comas-Vives,[a] Matthew P. Conley,[a] Aaron J. Rossini,[b] Anne Lesage,[b] Lyndon Emsley,[b,*] Christophe Copéret[a,*]

[a]Laboratory of Inorganic Chemistry, ETH Zürich, CH-8093 Zürich, Switzerland. [b]Centre de RMN à Très Hauts Champs, University de Lyon (CNRS/ENS Lyon/ UCB Lyon), 69100 Villeurbanne, France.
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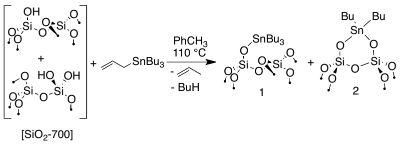
Silica is used for 'single-site' heterogeneous catalysts that have organometallic functionalities grafted on a silica surface with controlled silanol density.[1] Here, the reaction of highly dehydroxylated silica with allyltributylstannane as a probe molecule for the detection of silanol sites is described. We characterized the tin-functionalized silica by Dynamic Nuclear Polarization solid-state NMR spectroscopy (DNP SENS)[2] and the peaks were assigned using computational calculations. The results agree with the tin complex in two well-defined environments, the first being a monografted $[(\equiv SiO)SnR_3]$ and the second being a bis-grafted $[(\equiv SiO)_2SnR_2]$ (**2**) species corresponding to a vicinal dislanol group. The latter result implies that the silica surface is modified upon grafting converting geminal to vicinal silanols, evidencing the dynamic behavior of silica.



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Inorganic and Coordination Chemistry **IC08**

Mechanistic Studies related to Nickel-Catalyzed Alkyl-Alkyl Cross Coupling Reactions

Jan Breitenfeld[1] and Xile Hu[1]

[1]Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland

Mechanistic studies of alkyl-alkyl Kumada-type cross-coupling reactions of nonactivated alkyl halides by the Ni-chloride complex $[(^{Me}N_2N)Ni\text{-}Cl]$ are presented.[1] Radical clock experiments show that coupling is proceeding through a radical-chain rather than a radical-rebound sequence. Moreover, a 2nd order dependence on Grignard in the turnover-determining step is observed. Based on this, a μ-alkyl bridged nickel magnesium species is proposed to be a key intermediate.

Isomerization and olefin exchange experiments demonstrate that β-H elimination is kinetically viable, but thermodynamically unfavorable in $[(^{Me}N_2N)Ni\text{-}alkyl]$ complexes.[2] The isomerization passes through an $[(^{Me}N_2N)Ni\text{-}H]$ intermediate, which can be isolated by reaction of $[(^{Me}N_2N)Ni\text{-}OMe]$ with Ph_2SiH_2.[3]

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Inorganic and Coordination Chemistry **IC09**

Non-native Analogs of a Wheat Metallothionein

Katsiaryna Tarasava, Eva Freisinger

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Metallothioneins (MTs) are small cysteine-rich proteins, involved in metal homeostasis, detoxification and scavenging of reactive oxygen species. The E_c-1 MT from *T.aestivum* (common wheat) consist of two domains, γ and β_E [1,2]. The two metal ions of the γ-domain form a Zn_2Cys_6 cluster (Fig. 1).

(1) Interaction of the γ-E_c-1 domain with Cu^I ions

We encountered that the γ-domain can also form a defined Cu^I_2-cluster *in vitro*. The cluster formation is investigated with UV/Vis, circular dichroism, and fluorescence spectroscopy. The same cluster is formed if Cu^I are titrated to the Zn_2- , Cd_2- or apo- γ-E_c-1 form.

(2) Influence of Cys→His mutations on the metal ion binding properties

In rare cases MTs can coordinate metal ions using histidine as ligand. Thiolates have a preference for Cd^{II}, whilst histidines preferentially coordinate Zn^{II}. We performed Cys→His mutations to increase the selectivity for Zn^{II} against Cd^{II} in the binding site. Using UV/Vis, circular dichroism, and NMR spectroscopy consecutive filling of metal binding centers in comparison to the wild-type protein was observed.

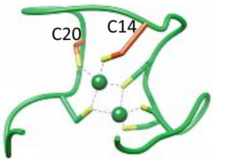

Fig. 1. Cd_2-γ-E_c-1 solution structure (Zn^{II} ions shown as spheres (pdb entry 2L62)).

Financial support from the Swiss National Science Foundation (SNSF-Professorship EF) and the CMSZH Graduate School is gratefully acknowledged.

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Inorganic and Coordination Chemistry **IC10**

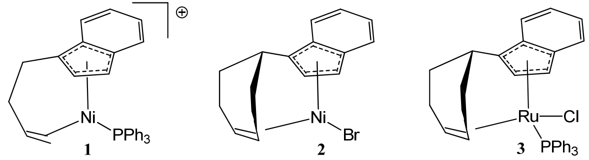
Indenyl Ruthenium and Nickel Complexes Bearing an Olefin Sidearm as a Steering Ligand.

Amos J. Rosenthal, Hansjörg Grützmacher

Laboratory of Inorganic Chemistry, Swiss Federal Institute of Technology, ETH Zürich, 8093 Zurich, Switzerland

The use of olefins as steering ligands has enabled the preparation of interesting complexes (e.g. rhodium coordinated aminyl radical)[1] and highly active catalysts[2]. The idea of combining olefin side arms with indenyl chemistry has been tried by Zargarian with complex **1**.[4] The olefin side arm enhanced the catalysis but was too labile for proper stabilization.

In the present study, we prepared a new ligand based on an indenyl and a trop (where trop is 5-H-dibenzo[a,d]cycloheptene-5-yl) moiety. Comlexes with nickel **2** and ruthenium **3** were prepared and characterized. Both complexes show interesting reactivity upon reduction with magnesium, the nickel form dimeric sandwich complexes and the ruthenium inserts into dialkylethers to form new ruthenium carbon bonds.



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Inorganic and Coordination Chemistry **IC11**

Photochemical Reduction of CO_2: Facts and Future

Shoubhik Das, Paul J. Dyson*, and Gabor Laurenczy*

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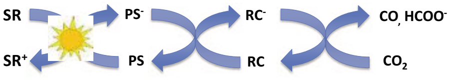
The demand for renewable energy sources that harvest solar energy is ever increasing. Of particular interest is the production of transportable fuels by artificial photosynthesis. Such technology might allow the energy from sunlight to be captured in parts of the world where food cannot be grown. An important step towards this goal, which has been studied by several chemists, is the photochemical reduction of carbon dioxide[1,2]. The first isolable reduction product of CO_2 is formic acid, HCO_2H, or its dehydration product, CO. The former is useful for hydrogen storage and delivery[3], and the latter can be used to generate hydrogen in the water–gas shift reaction[4].



SR= Sacrificial Reductant; PS= Photosensitizer; RC= Reducing catalyst

There have been a significant number of recent impressive accomplishments in the photochemical reduction of CO_2, especially through the development of inorganic and organometallic complexes[5]. But in most of the cases only CO has been produced. In this respect formation of formate via visible light mediated photocatalysis is still in their infancy. So hereby we are focusing on the formation of formate via visible light mediated photocatalytic reduction of carbon dioxide.

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Inorganic and Coordination Chemistry **IC12**

An Iridium (III) Hydride Pincer Complex Grafted on Mesoporous Silica as Single-Site Catalyst for Gas-Phase Olefin Hydrogenation

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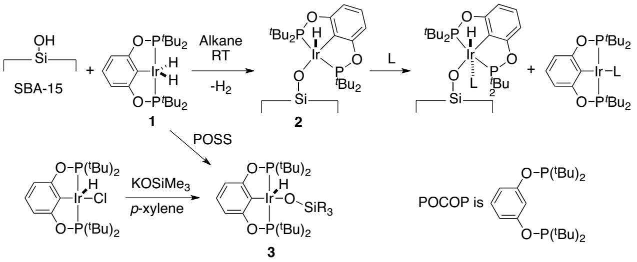
The dihydride complex [IrH_2(POCOP)] (**1**) [1] reacts with SBA-15 to give the coordinatively unsaturated, 16-electron hydride complex [IrH(O–SBA-15)(POCOP)] (**2**). This new grafting approach proceeds by formal reaction of a hydride ligand with surface silanols and elimination of dihydrogen. Solid state NMR spectroscopy and comparison with analogous soluble model complexes **3** suggest that **2** contains a coordinatively unsaturated square-pyramidal Ir(III) complex. This species reacts with ligands such as CO, ^{t}BuNC, and ethylene (L) to give the corresponding six-coordinate complexes or the product of reductive elimination, the Ir(I) species [Ir(L)(POCOP)].



Compound **2** is catalytically active without any activation step in the gas-phase hydrogenation of olefins. The catalytic reactions were performed in a batch reactor at room temperature (1 bar olefin, 1 bar H_2), the products were quantified by gas-phase ^{1}H NMR spectroscopy and recycling of the catalyst is also possible.

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Inorganic and Coordination Chemistry **IC13**

Impact of structural modifications of Vitamin B_{12} on its physico-chemical properties and the biological activity

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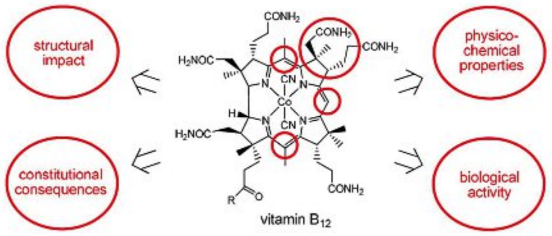
Cobalamins play an essential role in the metabolism of humans. Cellular uptake as well as the reactivity in B_{12}-dependent reactions are strongly related to the constitution and the electronic properties of the co-factor.[1] Our group investigates the impact of structural modifications of vitamin B_{12} on its physico-chemical properties and its biological activity.[2,3]

Recently, we reported biological studies with loop-modified derivatives.[4] Here, a group of novel modifications as well as their influence on physic-chemical properties and biological activity is presented.



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Inorganic and Coordination Chemistry **IC14**

A Novel synthetic pathway for the formation of water stable ^{99}Tc-NHC Complexes

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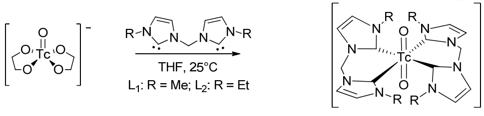
The structural versatility renders N-heterocyclic carbenes (NHCs) ideal for rational ligand design and has led to a drastic increase of their use in transition metal chemistry. Recently, Abram U. *et al.* have demonstrated that NHCs also form strong 99-technetium (^{99}Tc) - carbon bonds.[1,2] However, the reported synthetic procedure is limited to only two NHC types (dimethylimidazol-2-ylidene, 1,2,4-triazol-5-ylidene). To study a greater variety of NHC ligands we developed a more general synthetic pathway for the preparation of stable $^{99}Tc^{(V)}$-NHC complexes. This new approach overcomes the limitations of the established method and will broaden the scope of ^{99}Tc-NHC chemistry in the future. Following the new developed strategy, starting from $(NBu_4)[^{99}TcO(glyc)_2]$ (glyc = ethylene glycol), the first water stable ^{99}Tc-NHC complexes $[^{99}TcO_2(\mathbf{L_1})_2]^+$ ($\mathbf{L_1}$ = 1,1'-dimethyl-3,3' methylenediimidazoline-2,2'-diylidene) and $[^{99}TcO_2(\mathbf{L_2})_2]^+$ ($\mathbf{L_2}$ = 1,1'-diethyl-3,3'-methylenediimidazoline-2,2'-diylidene) have been prepared.



$[TcO_2(L_{1/2})_2]^+$

As demonstrated, generates this novel approach for the preparation of high valent ^{99}Tc complexes new opportunities in the field of organometallic $^{99(m)}$Tc chemistry and shows the great potential of NHCs as stabilizing ligands in this field.

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Inorganic and Coordination Chemistry **IC15**

Molecular Light-Upconversion Emission in Polynuclear Chrome(III)−Lanthanide(III) Complexes

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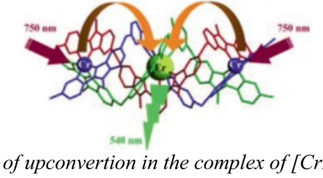
Near-Infrared (NIR) to visible light upconversion is a process in which photoexcitation in the NIR is followed by luminescence at a shorter wavelength in the visible. Upconversion has been regularly reported for trivalent lanthanide cations doped into low-phonon inorganic matrices, particularly for applications in bioanalyses, and solar energy conversion [1]. However, upconversion is prevented at the molecular level because of the high effective vibrational energy produced by organic ligands or solvent molecules, which efficiently relax 4f-4f transitions [1]. The trinuclear complex $[CrErCr(\mathbf{L})_3]^{9+}$ is the single example of molecular upconversion, in which NIR irradiation sensitizes the green upconverted $Er(^4S_{3/2} \rightarrow {}^4I_{15/2})$ emission. Theoretical calculations suggest that the latter unprecedented upconversion originates from the storage of NIR photons onto long-lived strong-field Cr^{III} sensitizers [2]. We report here on the quantitative experimental characterization of the energy transfer upconversion mechanism operating at the molecular level.



Schematic of upconvertion in the complex of $[CrErCr(\mathbf{L})_3]^{9+}$

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Inorganic and Coordination Chemistry **IC16**

Supramolecular Organization and Magnetic Properties of Mesogen-Hybridized Mixed-Valent Manganese Single Molecule Magnets $[Mn^{III}_8Mn^{IV}_4O_{12}(L_{x,y,z\text{-}CB})_{16}(H_2O)_4]$

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Single molecule magnets (SMM) may be considered for the construction of future integrated nanodevices, provided however that some degree of ordering is imparted to these molecules (surfaces nanostructuration). Combining such nano-objects with liquid-crystalline orderings to control their assembly and to potentially address them individually therefore appears as one promising strategy. Four mesomorphic, mixed-valent $[Mn^{III}_8Mn^{IV}_4O_{12}(L_{x,y,z\text{-}CB})_{16}(H_2O)_4]$ SMM, differing in the number of liquid-crystalline promoters, were synthesized, and their self-organizing and magnetic properties were investigated. [1] The influence of the peripheral modifications, and precisely how supramolecular ordering and magnetic properties may be affected by the evolution of the proto-mesogenic cyanobiphenyl-based ligands substitution pattern, was explored. Small-angle X-ray scattering studies revealed that all of the hybridized clusters self-organize into room-temperature bilayer smectic phases, mandated by the specific mesogenic functionalization and that the polymetallic cores are further organized according to a short-range pseudo-2D lattice with hexagonal and/or square symmetry. All mesomorphous hybridized dodecamanganese complexes still behave as SMM: they exhibit blocking of the magnetization at about 2.6 K as evidenced by the occurrence of frequency-dependent out-of-phase ac susceptibility signals as well as an opening of the hysteresis cycle with coercive fields varying between 0.13 and 0.6 T, depending on the surface ligands topology. Comparison of the magnetic properties within this series reveals intricate correlations between the structural features of the mesomorphous molecule magnet.

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Inorganic and Coordination Chemistry **IC17**

Liquid Electrolytes for Anion Transport in Fluoride Batteries

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There exist many different battery concepts based on reversible shuttle of charge transfer ions (e.g. Li$^+$, Na$^+$, Mg^{2+}, H$^+$, OH$^-$) which are currently being investigated and also already in commercial use.

Another interesting approach for batteries would be to use the outstanding potential of fluorine with its high electronegativity. During formation of metal fluorides a large change in free energy can be observed, this leads to high theoretical voltages in electrochemical cells. The functionality of such secondary fluoride ion batteries was recently demonstrated by A. Reddy and M. Fichtner [1].

To optimize the fluoride transport at room temperature it is necessary to develop liquid electrolytes, which can assure mass- and charge-transfer between both electrodes.

A problem in the synthesis of electrolytes is the interaction of the cations with the halides, which act as charge carriers, for example, through the formation of hydrogen-bonds. One way to avoid such interactions would be to use large ligand molecules, which will “wrap” the cationic molecules and inhibit interactions with the anions.

New compounds will be presented for the synthesis of liquid fluoride electrolytes based on this approach.

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Inorganic and Coordination Chemistry **IC18**

Water-soluble organometallic assemblies containing photo-switchable ligands

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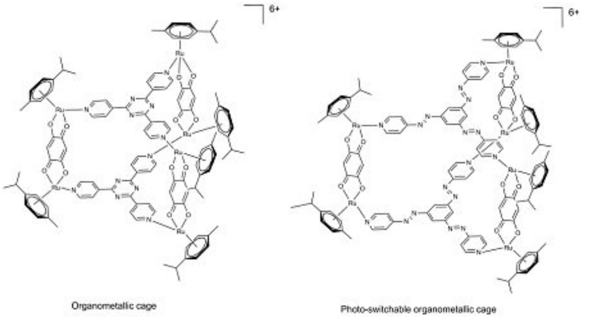
Research in our group is focused on the synthesis of organometallic cages for biological applications. These cages are able to encapsulate and deliver various molecules such as drugs[1] or photosensitizers[2] to cells. Herein, diazo ligands and dithienylethene derivatives are used to synthesize ruthenium metalla-cages similar to those already prepared in our group. The interesting feature of these molecules is the *Z/E* isomerization[3] or the cyclization reaction[4] which occur under ultraviolet irradiation, making possible changes in the conformation of the assembly, and thus facilitating the releasing control of the guest molecule *via* an opened-closed switchable system.



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Inorganic and Coordination Chemistry **IC19**

Cobalt-based spinel catalysts for visible-light-driven water oxidation

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Nature's most powerful water oxidation catalyst, the {Mn$_4$Ca} cluster core of photosystem II (PSII), has inspired the development of various robust and low-cost oxide compounds with similar structural motifs.[1,2] Until now, most studies are focused on either Co or Mn binary oxides, whereas considerably less is known about mixed Co/Mn-WOCs.[3] We thus started a systematic study into the visible-light-driven water oxidation activities of Co$_x$Mn$_{3-x}$O$_4$ (x = 0, 1, 2, 3) spinel oxides. The water oxidation activity for hydrothermally synthesized spinels was found to be $Co_3O_4 > Co_2MnO_4 > CoMn_2O_4 > Mn_3O_4$. Based on a wide range of characterizations (PXRD, BET, SEM, Raman, UV/vis...), we provide several possible explanations concerning morphology, structure and surface effects. Higher water oxidation activity of the Co-rich spinel oxides may be due to their smaller particle sizes. Tetragonal distortions of the Mn-rich spinels CoMn$_2$O$_4$ and Mn$_3$O$_4$ might furthermore reduce the efficiency of the cubane-related active centers in comparison with the cubic Co-rich spinels. Finally, higher Co contents might accelerate the reaction kinetics through their enhanced interaction with water molecules. We now implement these results for further optimization and post-treatment strategies to develop robust spinel WOCs.

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Inorganic and Coordination Chemistry **IC20**

Thiolato-Bridged Arene Ruthenium Complexes with High Anticancer Activity

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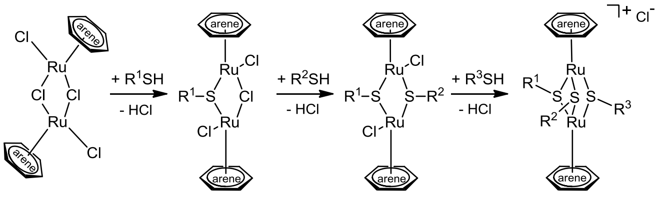
The dinuclear complexes of the type [(arene)$_2$Ru$_2$(SR)$_3$]$^+$ have been found to be among the most active ruthenium compounds with *in vitro* anticancer properties [1,2]. This can be partially explained by their catalytic potential for the oxidation of glutathione [2,3].



We have developed a new approach to the synthesis of diruthenium thiolato-bridged complexes, which enables the selective preparation of mono-, di- or trithiolato-bridged complexes with different substituents R^1, R^2 and R^3. By this method, lipophilicity, redox properties and molecular size can be designed to measure, thus permitting the optimization of anticancer activity.

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Inorganic and Coordination Chemistry **IC21**

Towards efficient solid-state dye sensitized solar cells (DSSCs)

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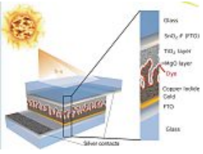
CH4056-Basel

Dye sensitized solar cells (DSSCs) are a promising alternative to conventional silicon based photovoltaic devices due to their ease of fabrication and low costs. Solid-state DSSCs, although not yet being as efficient as their liquid electrolyte counterparts, do not suffer from the problem of solvent evaporation and hence promise better long term stability.

Currently, our group is investigating the fabrication of solid-state DSSCs based on poly(3,4-ethylenedioxythiophene) and copper(I)iodide as hole conductors. Progress in this field will be reported including the use of a variety of 2,2'-bipyridine-based anchoring ligands and copper(I) dyes.



Layer structure of a solid state DSSC

Inorganic and Coordination Chemistry **IC22**

Tris(carboxyethyl)phosphine (TCEP) as new irreversible electron donor in photocatalytic H_2 production

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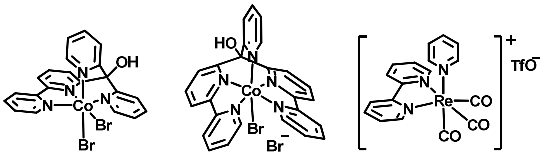
Polypyridyl complexes [CoBr(TPy)]Br (**1**) and [CoBr(aPPy)]Br (**2**) have excellent properties as water reducing catalysts (WRC) in photocatalytic H_2 production.[1,2] Turnover numbers up to 11'000 (H_2/Co) were achieved in H_2O with $[Re(CO)_3(BPy)Py]OTf$ (**3**) as photosensitizer and ascorbic acid (AscOH) as sacrificial electron donor (ED). This longevity of this system is limited by dehydroascorbic acid (DHA), leading to self-inhibition of catalysis.[3] Therefore, TCEP was introduced as a new, irreversible ED for photocatalytic water reduction. TCEP itself showed low H_2 evolution, however, it does regenerate *in situ* AscOH from DHA, increasing H_2 production significantly and leading the reaction to run to completion with respect to TCEP.



1 **2** **3**

Scheme 1: WRC **1** and **2** along with photosensitizer **3**.

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Inorganic and Coordination Chemistry **IC23**

High-pressure NMR: A tool to study tin-catalyzed synthesis of organic carbonates from carbon dioxide and alcohols

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Organotin(IV) compounds are known to be efficient catalysts for the transformation of carbon dioxide into useful chemicals such as linear dialkyl carbonates, cyclic carbonates, and oxazolidone [1]. In the past, we showed in particular the positive role of diorganotin(IV) alkoxides, $R_2Sn(OR')_2$ (R = *n*-Bu, *tert*-Bu, Bz; R' = Me, Et, ^{i}Pr), as catalytic precursors for the direct carbonation of alcohols (Eq. 1) [2].

$$CO_2 + 2\,ROH \longrightarrow (RO)_2CO + H_2O \qquad (1)$$

Although several CO_2- and carbonate-adducts have been characterized by X-ray crystallography [3], the reaction mechanisms remain still unclear. In this aim, high pressure NMR spectroscopy experiments, under CO_2 pressure and in deuterated alcohols, were achieved [4]. This project is supported by the Swiss Academy of Engineering Science (SATW) and the French Ministry of Foreign Affairs in the frame of the Germaine de Staël program (projects No. 2013-33 and No. 28187TB, respectively).

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Inorganic and Coordination Chemistry **IC24**

Liquid-crystalline properties of anthracene-core dendrimers in combination with arene ruthenium metallocycles

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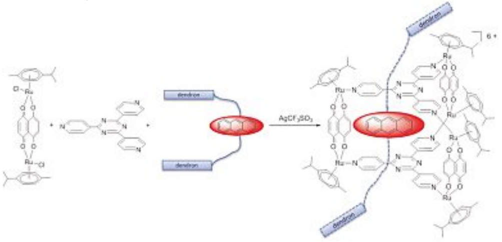
Self-organization of metallomesogens is of interest to combine properties of both metallic (optical electronic, magnetic) and mesogenic (low-dimensional structures, fluidity) parts [1]. A wide variety of metallomesogens have been generated to date using concepts from both coordination and supramolecular chemistries. Such diversity embraces simple to very intricate molecular systems. In our laboratory, pyrenyl-containing dendrimers have been combined with metallocycles, resulting in host-guest systems with interesting biological activities [2]. Hence, the association of anthracene-core dendrimers, which show mesomorphic properties, with arene ruthenium metallocages has been studied (Scheme 1).



Scheme 1. Encapsulation of anthracene-mesogens in metalloprism.

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Inorganic and Coordination Chemistry **IC25**

Silver captured in responsive polymer systems

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In the past, many different metals were used in supramolecular chemistry to synthesise metal-ligand-polymer systems. The building blocks are ligand-end capped oligomers and metal salts out of which the polymer is built up via solution-mixing. The metal (ion) serves as linker between two ligand-oligomer chains.

Contrary to this approach, the goal of my project is to capture a silver ion or nanoparticle. This should be accomplished with a ligand system that consists of an oligomer, such as tetraethylene glycol, which is end capped on both sides with pyridine units. This ligand should form a helical structure around the silver with both pyridine units coordinated to the same silver ion or nanoparticle. After completion of the first milestone, this pyridine unit will be modified by attaching a polymer chain that can work as a handle. By applying, for example, mechanical force, like ultra-sonication, the silver (ion) can be released (*Figure 1*) by the external trigger and used for catalysis or in medicine, where its antimicrobial properties are requested.

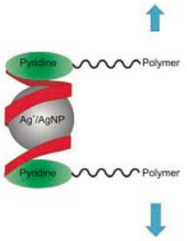

Figure 1: Schematic illustration of controlled silver release from a ligand-polymer system by applied force (arrows).

Inorganic and Coordination Chemistry **IC26**

Synthesis of organometallic assemblies from quinonoid zwitterions

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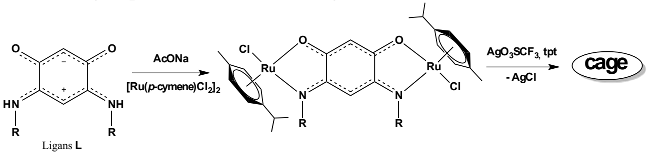
Following our previous work on metalla-assemblies,[1] a large cationic triangular metalla-prism $[Ru_6(p\text{-cymene})_6(tpt)_2(L)_3]^{6+}$, incorporating (*p*-cymene) ruthenium building blocks, bridged by *N,N'*-R,R-2-amino-5-alcoholate-1,4-benzoquinonemonoiminium zwitterionic ligands (L),[2] and connected by two 2,4,6-tri(pyridin-4-yl)-1,3,5-triazine (tpt) subunits allows the encapsulation of various guest molecules. These cationic cages and cationic host-guest systems have been isolated as their triflate salts. The formation of the cages was confirmed by NMR spectroscopy. The properties of these systems were studied in solution by acid-base titrations, allowing the determination of the pH needed to break the cages. Moreover, the solubility and property of the cages can be modified by introduction of different functional groups on the zwitterionic ligand.



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Inorganic and Coordination Chemistry **IC27**

Clathrochelate-based Bipyridyl Ligands of Nanoscale Dimensions

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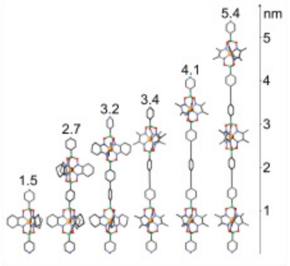
Institut des Sciences et Ingénierie Chimiques, Ecole Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland

The structure and function of a supramolecular assembly is determined by the building blocks from which it is derived. Consequently, control over the steric and functional characteristics of these building blocks is an imperative aspect of supramolecular chemistry. We have demonstrated that boronic acid-capped clathrochelates are versatile scaffolds for the synthesis of long and rigid bipyridyl ligands, one of the most common structural motifs in metallasupramolecular chemistry.[1] Bipyridyl ligands between 1.5 and 5.4 nm in length can be obtained in one or two steps from simple starting materials. These building blocks are compatible with metallasupramolecular chemistry as evidenced by the synthesis of a discrete metallamacrocyclic structure and a heterometallic, three-dimensional metal–organic framework.



- ✓ Rigid
- ✓ Long
- ✓ Easy to synthesise
- ✓ Scope for structural and functional modification

[1] Matthew D. Wise, Albert Ruggi, Mirela Pascu, Rosario Scopelliti, Kay Severin, *Chem. Sci.* **2013**, *4*, 1658.

Inorganic and Coordination Chemistry **IC28**

Novel $\{fac\text{-}Re(CO)_3\}^+$ Based Photosensitizers for Photocatalytic H_2-Production

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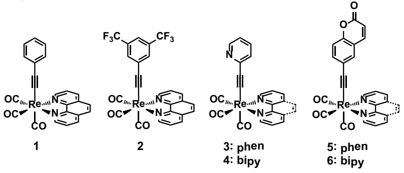
Due to their interesting luminescent properties, $[fac\text{-}ReX(CO)_3(N\cap N)\}^+$ type complexes are investigated as photosensitizers in photocatalytic reactions.[1-3] We recently developed a series of rhenium (I) complexes with the general formula $[ReX(CO)_3diimine]$ showing high activities in photocatalytic H_2-production.[3] In order to increase the stability of the axial X-substituent, and hence, to influence catalytic longevity in photocatalytic H_2-formation as well as their photophysical properties, several novel complexes with X=acetylene moieties have been prepared, characterized (scheme 1) and subjected to photocatalysis studies.[4]



Scheme 1: Six photosensitizers showing high activitiy in H_2-production

[1] Kurz, P.; Probst, B.; Spingler, B.; Alberto, R., *Eur. J. Inorg. Chem.* **2006,** 2966-2974.

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Inorganic and Coordination Chemistry **IC29**

Dynamic Ligand Exchange in Arene-Ruthenium Metalla-Rectangles

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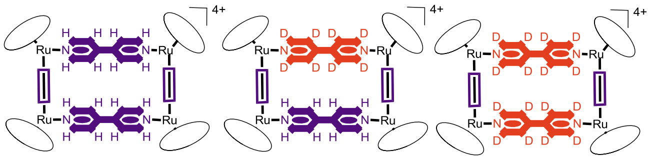
Arene-ruthenium metalla-assemblies constructed *via* coordination of ruthenium units and organic-linkers have attracted considerable attention due to their intriguing structure and potential applications.[1] While most investigations have largely focused on the synthetic routes and the structural features of these supramolecular assemblies, reports dealing with the dynamic characteristics of such structures are absent. Isotope labeling is an appropriate tool for characterizing dynamic exchange in metalla-supramolecular assemblies.[2] With this technique, the dynamic ligand exchange process in arene-ruthenium metalla-rectangles as well as the subsequent equilibrium under thermodynamic control were successfully studied. Moreover, on the basis of quantitative mass spectral results, the kinetics of the exchange process will be also discussed.



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Inorganic and Coordination Chemistry **IC30**

Homoleptic and heteroleptic bis(2,2':6',2''-terpyridine)chromium(III) complexes

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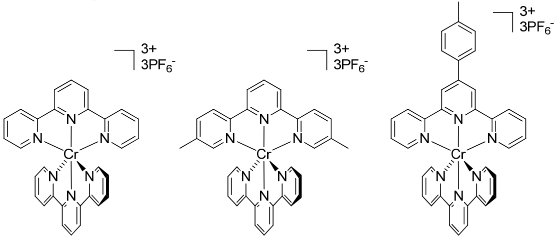
We present the synthesis and characterisation of a series of ionic homoleptic and heteroleptic bis(2,2':6',2''-terpyridine)chromium(III) complexes. 2,2':6',2''-Terpyridine (tpy) and derivatives thereof function as chelating tridentate ligands. To the best of our knowledge, heteroleptic bis(2,2':6',2''-terpyridine)chromium(III) complexes have not previously been reported in the literature. Since chromium is relatively abundant in the Earth's crust and therefore also cheap, chromium(III) compounds could be an alternative to scare metals such as ruthenium or iridium for DSC (Dye-sensitized Solar Cell) or LEC (Light Emitting Electrochemical Cell) applications since their photophysical properties are amenable to such functions. We report a series of such complexes, structures of which are confirmed by X-ray analysis. In neutral and acidic aqueous solutions the complexes are stable, whereas they undergo changes in a basic environment. This decay can be monitored by a colour change of the solution and the detection of free ligand after treatment with a base.



Inorganic and Coordination Chemistry **IC31**

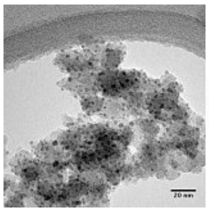
Preparation and Characterisation of Small Ag Nanoparticles Supported on Fully Passivated Silica

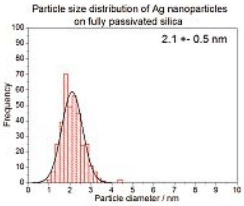
Emma Oakton, Daniel Levine, Eva Zocher and Christophe Copéret

ETH Zürich, Wolfgang-Pauli Str. 10, 8093 Zürich, Switzerland

Supported silver nanoparticles have shown catalytic activity towards many reactions, particularly the oxidation of ethylene to the corresponding epoxide. The catalytic performance of such materials are dependant on both the metal particle size and support and therefore a tremendous effort is being made in addressing these issues. Recently it was shown that it is possible to control the growth of Au nanoparticles and their interface with a silica support via the controlled grafting of an Au(I) amide followed by mild hydrogen treatment.[1]

Here we report that small Ag nanoparticles supported on fully passivated silica can be prepared in a two-step process: 1) controlled funtionalisation of silica with silver(I) bis trimethylsilyl amide and 2) subsequent treatment under hydrogen at 300 °C. This approach produces small Ag nanoparticles with narrow size distribution supported on a fully passivated silica surface.





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Inorganic and Coordination Chemistry **IC32**

Isoelectronic thiolate based metathesis catalysts

F. Allouche, V. Mougel, W. Grüning and C. Copéret

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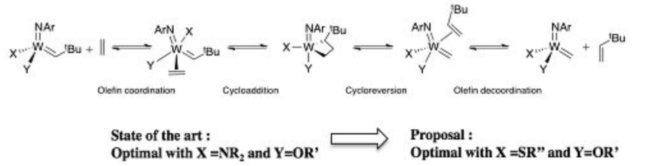
Wolfgang-Pauli-Strasse 10, 8093 Zurich, Switzerland

Over the last 50 years, in both industry and research, alkene metathesis has become a key reaction. Homogeneous catalysis has shown that well-defined alkylidenes in high oxidation state (typically d^0) having electron-withdrawing ligands were highly efficient metathesis catalysts. The coveart-being the metal need to be stabilized by rather large ligand, hence the design of bulky arylimido based systems by Schrock et al.[1]. More recent work involving surface chemistry[2] (molecular heterogeneous catalysis) combined with computational studies[3] made it possible to understand the structure-activity relationship of d^0-metal based alkene metathesis catalysts. A key point for reactivity is to have a d^0-metal center having two very different ligands (one weak and one strong σ-donor ligand). This favors low energy barriers for coordination of the olefin, the subsequent [2+2]-cycloaddition and also destabilizes the metallacyclobutane intermediates.

Here, we describe a series of alkene metathesis catalysts with thiolate ligands, which are strong σ-donor ligands and whose steric hindrance can be easily tuned.



State of the art :
Optimal with X =NR_2 and Y=OR'

Proposal :
Optimal with X =SR'' and Y=OR'

[1] R. R. Schrock et al., *J. Am. Chem. Soc.*, **1990**, 112, 3875.
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[3] X. Solans-Monfort et al., *J. Am. Chem. Soc.*, **2010**, 132, 7750-7757.

Inorganic and Coordination Chemistry **IC33**

Synthesis and Characterization of Mesostructured Hybrid Silica Materials and their Use as Polarization Matrices in SS DNP NMR

Martin Schwarzwälder,[1] D. Gajan,[1,2] M. P. Conley,[1] W. R. Grüning,[1] A. J. Rossini,[2] A. Zagdoun,[2] M. Lelli,[2] M. Yulikov,[1] G. Jeschke,[1] C. Sauvee,[3] O. Ouari,[3] P. Tordo,[3] L. Veyre,[4] C. Thieuleux,[4] A. Lesage,[2] L. Emsley,[2*] and C. Copéret.[1*]

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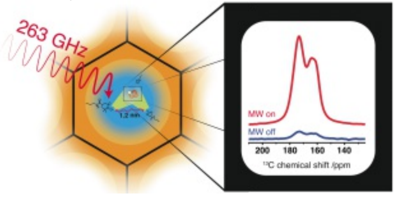
2. Centre de RMN à Très Hauts Champs, Université de Lyon, France
3. Institut de Chimie Radicalaire, Aix-Marseille Université, France
4. Université de Lyon, C2P2, CPE Lyon, France.

The synthesis of mesostructured hybrid silica materials with homogeneously distributed organic moieties was reported using sol-gel technique. We have established the application of SS DNP NMR to investigate organic species located on surfaces of mesopourous silica materials.[1]

Here, we show the synthesis of mesostructured hybrid silica materials as a platform material. By two steps, we were able to incorporate different radicals. We prove that the method is robust in terms of conversion by CW EPR and can even show that radicals are distributed homogeneously within the material. The use of this material in SS DNP NMR shows enhancements up to 40 that is significantly better than the use of the same radical in solution.



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Inorganic and Coordination Chemistry **IC34**

C_2-Symmetric N_2P_2-Macrocycles and their Fe(II) and Ru(II) Complexes

Raphael Bigler and Antonio Mezzetti*

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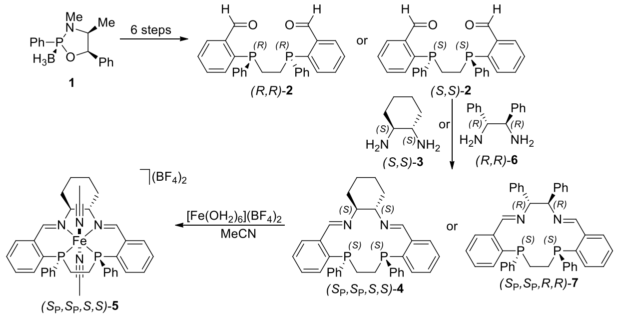
Following our interest in open-chain and macrocyclic PNNP ligands,[1,2] we prepared the new synthons *(R,R)*-**2** and *(S,S)*-**2** from Jugé's oxazaphospholidine borane **1**. Both *(R,R)*-**2** and *(S,S)*-**2** were obtained in enantiomerically and diastereomerically pure form after recrystallization.



The condensation of *(S,S)*-**2** with the chiral diamines *(S,S)*-**3** and *(R,R)*-**6** gave the C_2-symmetric macrocyclic PNNP ligands (S_P,S_P,S,S)-**4** and (S_P,S_P,R,R)-**7**. Both ligands were reacted with suitable Fe(II) and Ru(II) precursors to give the corresponding [Fe(NCMe)$_2$(PNNP)](BF$_4$)$_2$ and [RuCl$_2$(PNNP)] complexes. Depending on the ligand and the metal, either a *cis-β* or a *trans* configuration is observed. The application of these complexes in asymmetric catalysis will be reported.

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Inorganic and Coordination Chemistry **IC35**

Chemical design of infrared-active Pb/Cd chalcogenide nanocrystal heterostructures

Loredana Protesescu[1,2], Maksym Kovalenko[1,2]

[1]ETH Zürich Laboratory of Inorganic Chemistry, Wolfgang-Pauli-Str. 10, 8093 Zurich, SWITZERLAND
[2]EMPA - Swiss Federal Laboratories for Materials Science and Technology, Ueberlandstrasse 129 CH-8600 Dübendorf, SWITZERLAND

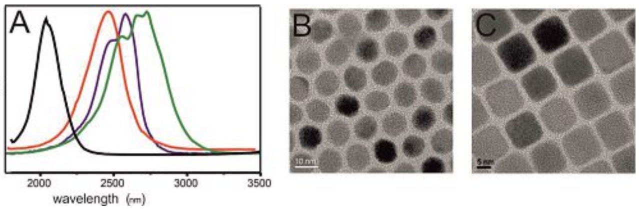


Figure 1. (A) Size-dependent hotoluminesce spectra of PbTe colloidal nanocrystal quantum dots (d=8-15 nm). (B, C) TEM images of spherical and cubic PbTe nanocrystals.

To date, optoelectronic devices based on colloidal quantum dots have been restricted to the visible or near-infrared spectral regions, while very limited progress has been achieved at the mid-infrared wavelengths beyond 2500nm. Lead chalcogenides in a quantum-size state are among the most promising materials for this purpose due to their narrow bulk bandgaps. Our present focus is on PbE/CdE chalcogenide heterostructures (E=S, Te). Unique features of these nanostructures are nearly complete immiscibility of rock-salt PbE and zinc-blende CdE, favorable band alignments, and coherent interfaces for low-index facets. Herein we present PbS/CdS core-shell with thick and uniform shells of 2-4 nm, yielding stable and narrow photoluminescence. Furthermore, we report PbTe/CdTe nanoheterostructures tuned for the mid-IR spectral region.

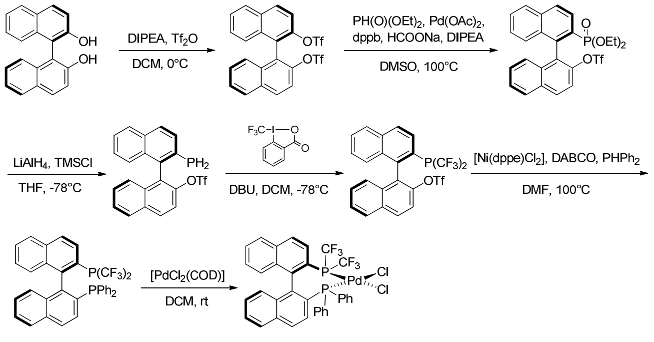
Inorganic and Coordination Chemistry **IC36**

Towards a new class of P-trifluoromethylated BINAP-derived ligands

Rima Drissi, Antonio Togni

Department of Chemistry and Applied Biosciences, Swiss Federal Institute of Technology, ETH Zürich, CH-8093 Zürich, Switzerland

The synthesis of a P-trifluoromethylated BINAP ligand was initially achieved in our group in five steps from *(R)*-BINOL. The coordination chemical properties of this first representative of a new class of BINAP ligands was determined by X-ray diffraction of a palladium(II) complex[1].



This breakthrough paved the way towards a new class of trifluoromethylated BINAP ligands. Part of our research is currently focused on the expansion of this novel class of ligands by preparing various derivatives, monodentate as well as bidentate, and to assess their potential in asymmetric homogeneous catalysis.

[1] N. Armanino, R. Koller, A. Togni, *Organometallics* **2010**, *29*, 1771.

Inorganic and Coordination Chemistry **IC37**

Activation of nitrous oxide by C-nucleophiles

Alexander G. Tskhovrebov and Kay Severin

Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne,
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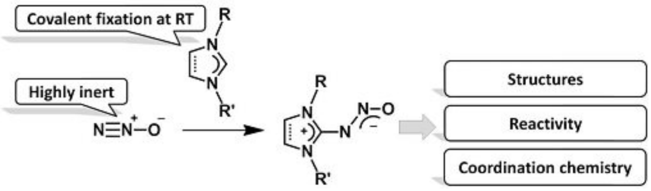
Nitrous oxide is the main ozone-depleting substance nowadays, and it is around 300 times more potent greenhouse gas then CO_2. In addition, N_2O is an appealing oxidant due to its thermodynamic potency and environmentally friendly nature (the only by product in oxygen atom transfer reactions is N_2).

Recently, we discovered that N-heterocyclic carbenes are able to fix N_2O and form stable adducts.[1] These adducts display unique reactivity as evidenced by different organic and organometallic transformations.[1,2]



Further, we discovered that some Grignard reagents and other C-nucleophiles are able to react with N_2O. This finding can potentially lead to the development of new synthetic processes that employ N_2O as a feedstock reagent.

[1] A.G. Tskhovrebov, E. Solari, M.D. Wodrich, R. Scopelliti, K. Severin, *Angew. Chem. Int. Ed.* **2012**, *51*, 232.
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Inorganic and Coordination Chemistry **IC38**

Dissecting cation-dependent RNA secondary structure formation by single-molecule fluorescence

Sebastian L.B. König, Danny Kowerko, Mokrane Khier, Mélodie Hadzic, Roland K.O. Sigel

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Winterthurerstrasse 190, CH-8057 Zurich

Group II introns are functional RNAs that catalyse their own excision (splicing). Splice site recognition is brought about by exon- and intron-binding sequences (EBS, IBS) and metal ions have been proposed to play a crucial role in their mutual recognition [1].

Here, we used single-molecule FRET to systematically assess the influence of various divalent metal ions along the Irving-Williams Series on EBS1*/IBS1* interaction [1]. We could show that the presence of divalent cations is crucial for EBS1*/IBS1* interaction to occur to a significant extent. However, inter-oligonucleotide affnity, as well as docking/undocking kinetics, varied by several orders of magnitude depending on the cation present. These observations could be explained through the intrinsic affinities of the cation towards the different metal ion binding sites encountered within RNA, which in turn allowed us to pinpoint the role of the cation in EBS1*/IBS1* interaction. This study not only validates smFRET for the systematic study of metal ion-mediated nucleic acid folding, it also shows that cation-dependent RNA folding may be explained by the coordination chemistry of the metal ion cofactor.

Funding: ERC starting grant (MIRNA 259092, to R.K.O.S.) and a Forschungskredit of the University of Zurich (57010302, to S.L.B.K.).

[1] Kruschel D., Sigel R.K.O., *J. Inorg. Biochem.* **2008**, *102*, 2147.

Inorganic and Coordination Chemistry **IC39**

Reaction kinetics and chemical equilibria in $HCOOH/CO_2 + H_2$ sytems

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Switzerland

Hydrogen storage is a critical question for the future hydrogen economy, from production to delivery, for energy conversion and applications. Recently, new results were reported on the use of carbon dioxide as a hydrogen vector via formation of formic acid (FA), in catalytic systems[1][2][3][4]. In order to overcome the thermodynamic barriers in the carbon dioxide hydrogenation reaction, amines can be utilized[5]. To realize a carbon-neutral "hydrogen cycle", H_2 storage and delivery could be described by equation (1) :

$$\mathrm{HCOOH \cdot amine} \rightleftharpoons \mathrm{H_2 + CO_2 + amine} \qquad (1)$$

High-pressure NMR spectroscopy was applied to study the reaction kinetics and chemical equilibria in equation (1) as a function of temperature, catalysts, concentrations and pressure; aiming the construction of a practical hydrogen storage device.

Acknowledgements: EPFL and Swiss National Science Foundation are thanked for financial support.

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Inorganic and Coordination Chemistry **IC40**

Anionic Iridium(III) Complexes for Light-Emitting Electrochemical Cells

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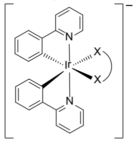
[2]Department of Chemistry, University of Basel, Klingelbergerstrasse 80, CH-4056 Basel, Switzerland

Light-emitting electrochemical cells (LEECs) are a relatively new and attractive option for solid-state lighting applications. These architecturally simple devices are built of a single emissive layer that is compatible with air stable electrodes and do not require rigorous encapsulation from the atmosphere. Since the first report of LEECs comprised of ionic transition metal complexes (iTMCs) in 1996, a majority of research has focused on cationic biscyclometalated iridium(III) complexes with a neutral ancillary ligand [1]. Anionic Ir complexes have been much less explored but the few reported examples containing monodentate ligands such as cyanide and thiocyanate have shown promising photophysical properties [2]. In an effort to expand upon this comparatively uninvestigated area we present the synthesis and characterization of new anionic Ir complexes with bidentate dioxolene and dithiolene ancillary ligands.



[1] K. M. Maness, R. H. Terrill, T. J. Meyey, R. W. Murray, R. M. Wightman, *J. Am. Chem. Soc.* **1996**, *118*, 10609.
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Inorganic and Coordination Chemistry **IC41**

Synthesis, characterisation and cytotoxicities of Ruthenium(α-amino acids) and Ruthenium(nucleotides) complexes

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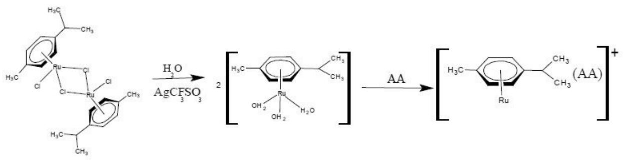
University of Bern, Freiestrasse 3, CH-3012 Bern, Switzerland

Over the years, there have been growing interests in developing new organometallic-based anticancer drugs. Gross considerations have been given to ruthenium-containing compounds because of their less severe side effects when compared with the toxicities encountered with their platinum counterparts, as well as their inability to address certain types of cancers. The use of NMR for characterisation of such compounds is indispensable in this search, as it provides useful information about their reactions with amino acids, DNA binding, as well as their stability and kinetics. In this research, different Ru-complexes of the general form [(η^6-*p*-cymene)Ru(AA)]$^+$ and [(η^6-*p*-cymene)Ru(N)]$^+$ [1] have been synthesized from [(η^6-*p*-cymene)$RuCl_2$]$_2$, with the aim of obtaining the potential cellular targets and also provide information about their cytotoxicities towards cancer cells. Likewise, their stability and reactivity with glutathione and nucleotides using various NMR techniques are discussed.



[1] Schluter A et al, Inorg. Chim. Acta. **2002**, 340, 35.

Inorganic and Coordination Chemistry **IC42**

Development and Characterization of Crystal-like Periodic Mesoporous Organosilicas Containing Bidentate Ligands

W. R. Grüning[1], A. J. Rossini[2], A. Zagdoun[2], A. Lesage[2], L. Emsley[2], C. Copéret[1].

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[2]CRMN, Université de Lyon, 69100 Villeurbanne, France.

Periodic Mesoporous Organosilicas (PMO) are an emerging class of hybrid organic inorganic materials [1]. PMO posses a high density of organic linkers that show a crystal like arrangement in the case of aromatics in their wall.[2] Modifying these linkers to contain potential ligand centers such as nitrogen and oxygen leads to well-defined surface ligands that can be functionalized to give metal-complexes on the surface, with possible applications in sensing, imaging and catalytic applications.

Here we will described the detailed characterization of phenylpyridine PMO (ppy-PMO) [3] containing materials. Dynamic Nuclear Polarization – Surface Enhanced NMR Spectroscopy allows us to rapidly acquire natural abundance nitrogen-15 spectra, and to distinguish resonances of outer an inner pyridine groups in a four-layered wall structure.[4] We will also discuss more recent advances towards development of PMOs incorporating bidendate ligands.

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Inorganic and Coordination Chemistry **IC43**

Towards Accumulative Electron Transfer in a Molecular Pentad

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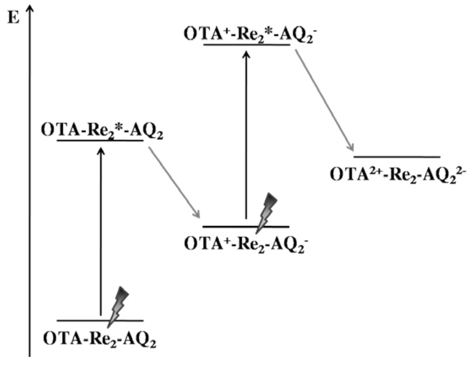
Nature's way of converting solar into chemical energy gives us a perfect blueprint to engineer a corresponding system ourselves [1].
Our goal is the construction of a wholly molecular system being comprised of two photosensitizers ([Re(bpy)$(CO)_3$(py)]$^+$) and acceptors (anthraquinones), as well as an oligotriarylamine (OTA) electron donor that can be oxidized several times. This system may then serve as a model to study charge separation and accumulation, the fundamental steps in photosynthesis.



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Inorganic and Coordination Chemistry **IC44**

Dinuclear arene Ru(II), Rh(III) and Ir(III) catalysts for the conversion of aldehydes to amides

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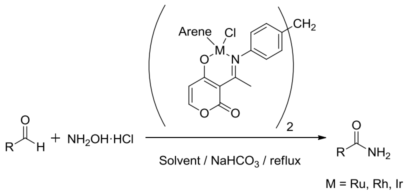
The amide bond is a key functional group in organic and biological synthesis. Beyond conventional methods toward the synthesis of amides, many alternative strategies have been reported. Among these alternative strategies, the transition-metal-catalyzed oxidative amidation of aldehydes with primary amines has been reported.[1] Recently, several groups have reported direct amide synthesis using ruthenium,[2] rhodium [3] and iridium[4] based catalytic systems. Here we synthesized and compared the catalytic activity of aldehyde to amide reaction using new arene ruthenium(II), rhodium(III) and iridium(III) complexes in a one-pot process in the presence of NH_2OH•HCl / $NaHCO_3$.



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Inorganic and Coordination Chemistry **IC45**

Asymmetric Hydrogenation of Ketones with Ru(II)/SNNS Catalysts:

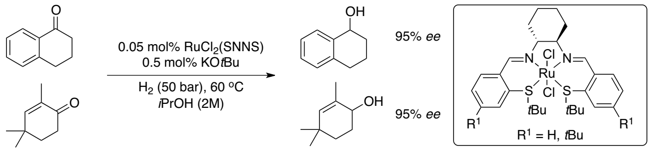
Chandan Dey,[a] Antonio Mezzetti,[a] and Francesco Santoro.[b]

[a]Department of Chemistry and Applied Biosciences, ETH Zürich, CH-8093 Zürich, Switzerland. [b]Firmenich SA, Corporate Process R&D Division, route des Jeunes 1, P.O.Box 239, CH-1211, Geneva 8, Switzerland.

The enantioselective hydrogenation of carbonyl groups has emerged as one of the most important synthetic reactions because it gives access to enantiopure alcholos that have vital importance in the pharmaceutical, fragrance, and food flavoring industries. The Ru(II)-catalyzed H_2-direct hydrogenation of carbonyl groups has gained importance not only in academic settings but also in industrial applications due to the environmental and economical friendliness of the protocol.

Firmenich has developed a range of air- and moisture-stable, phosphine-free [$RuCl_2$(SNNS)] complexes (where SNNS is a chiral tetradentate ligand with a S_2N_2 donor set) that were efficiently applied as precatalysts in the asymmetric H_2-hydrogenation of a broad range of prochiral ketones with S/C ratios of up to 10^6. The chiral alcohols were obtained in high yield and good to excellent enantioselectivity.[1-2]

We are currently preparing the corresponding ruthenium-hydride complexes to investigate the nature of the catalytic reactive species and to better understand the reaction mechanism.



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Inorganic and Coordination Chemistry **IC46**

PHOTOINDUCED ELECTRON TRANSFER IN TRIARYLAMINE-BORARYL-RUTHENIUM SYSTEMS

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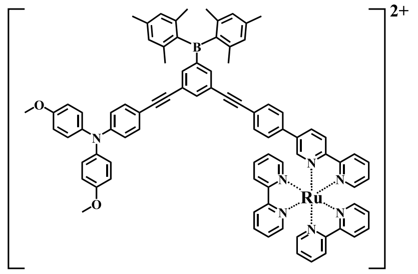
Luminescence of organoboron compounds can be quenched upon addition of fluoride ions[1]. Therefore they can be used as sensors[2].

Our goal is to synthesize and to explore a molecule comprised of a triarylamine donor (D), a bridge containing a dimesitylboron unit, and a ruthenium acceptor (A) [see picture].



Upon photoexcitation we expect electron transfer from D to A. We plan to explore how fluoride binding to the boron unit affects the electron transfer from D to A.

The binding of fluoride anions to the boron atom can easily be followed by optical absorption as well as by luminescence spectroscopy. We plan to explore whether intramolecular long-range charge transfer processes in donor-bridge-acceptor compounds with dimesitylboryl bridging units could be controlled by addition of fluoride ions.

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Inorganic and Coordination Chemistry **IC47**

How does RNA bind B_{12}: A chemical investigation

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How can two large and highly complex biomolecules such as RNA and coenzyme B_{12} interact specifically and with high affinity? This is the question we are addressing with our investigation on the binding mechanism between the *btuB* riboswitch of *E. coli* and its ligand coenzyme B_{12}.[1]

The fact that the *btuB* riboswitch is highly selective towards specific derivatives of the B_{12}-family, which however can strongly differ in their general structure [1,2], leads to the question which are the structural requirements on the B_{12}-molecule for this interaction.

We have synthesized three series of B_{12}-derivatives with modifications at the main functional sites. Modifications on the corrin ring sidechains, such as acids and amides, are aimed to study the H-bonding and electrostatic pattern. Modifications on the upper axial ligand include also platinum(II)-linked nucleobases, which can give insight in possible base-pairing and/or stacking. A third group comprises derivatives with a peptide backbone replacing the sugar phosphate at the lower loop.[3] Our experiments confirmed the importance of the upper moiety, preferentially being adenosyl, for a high affinity to the RNA. The presence of acid or amide groups in the sidechains leads to differences in the reorganization of the RNA. Finally, the derivatives carrying the peptide loop show a strong dependence of the stereochemistry. In fact, only one isomer of this series was shown to switch the riboswitch, although with alterations and with lower affinity.

Financial support by the European Research Council (ERC starting grant to R.K.O.S.), the Swiss State Secretariat for Education Research and Innovation (COST Action CM1105), and the University of Zurich is gratefully acknowledged.

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Inorganic and Coordination Chemistry **IC48**

Neocuproine Based Copper Dyes for Dye Sensitized Solar Cells

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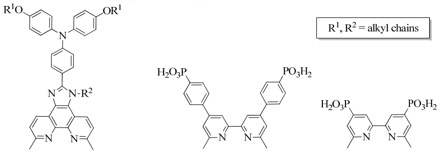
Dye sensitized solar cells (DSSCs) are of great interest as a valuable alternative to the commercial silicon solar cells. Copper(I)-based dyes have shown promising performances in DSSCs and are interesting candidates for low-cost solar cells.

A straight forward approach to obtain TiO_2 bound heteroleptic copper(I) complexes is by ligand exchange between homoleptic copper(I) complexes and TiO_2 anchored 2,2'-bipyridine ligands [1]. Anchoring ligands functionalized with phosphonic acids rather than carboxylic acids have been shown to be more efficient for copper complexes [2].



1 **2** **3**

Homoleptic copper (I) complexes with neocuproine based ligands of type 1 are exchanged with anchoring ligands 2 and 3. The influence on the performance of the alkyl chain length in the surface-bound heteroleptic complexes are being studied in DSSCs using I^-/I_3^- and $Co^{2+/3+}$ electrolytes. Furthermore, additives such as chenodeoxycholic and stearic acids in the anchoring step are being tested.

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Inorganic and Coordination Chemistry **IC49**

Bioactivity of Vitamin B_{12} Derivatives

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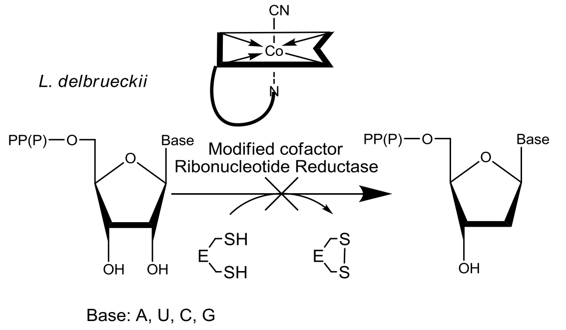
Vitamin B_{12} cofactors are essential for cell growth in mammals and most other forms of life.[1] For this reason, fast proliferating cancer cells are strong consumers of B_{12}.[2] We suggest the development of B_{12} derivatives as potential inhibitors of catalytical cycles regulated by B_{12} cofactors.



Herein, we present the development and study of new B_{12} surrogates.[3] Bacterial growth tests will give insights into structure-activity relationships..

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Inorganic and Coordination Chemistry **IC50**

A General and Simplified Approach for the synthesis of uniform and monodisperse Indium, Bismuth, Copper and Antimony Nanocrystals

Meng He, Maksym Kovalenko

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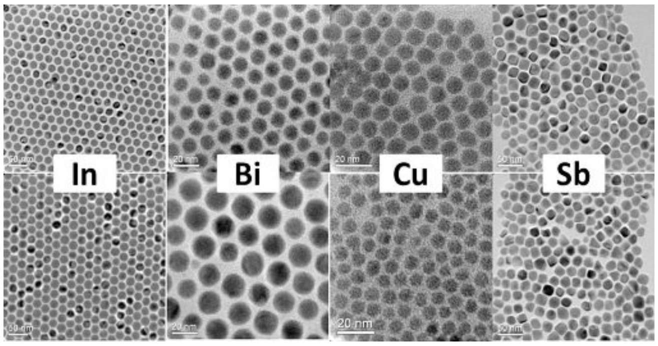
EMPA-Swiss Federal Laboratories for Materials Science and Technology, CH-8060 Dübendorf, Switzerland

A simple and general approach for the synthesis of uniform and monodisperse Indium, Bismuth, Copper and Antimony nanocrystals is reported. Metal chloride, instead of organometallic precursor, is used in the in-situ synthesis, which simplified the procedure and reduces the costs. Particle-size controllable synthesis is also achieved by using different time, temperature and amount of precursor.



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Inorganic and Coordination Chemistry **IC51**

Cold Plasma Surface Alteration of Activated Carbon as an Adsorbent of Organic Chlorinated Compound(s)

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Lab. für Anorganische Chemie, HCI, Wolfgang-Pauli-Str. 10, ETH Zürich, Zürich 8093.

Two organochlorinated insecticides chlordecone (CLD) and β-hexachlorocyclohexane (β-HCH) had been detected in Guadeloupe and Martinica after their extensive use to control the banana weevil Cosmopolites sordidus from 1972 to 1993 [1]. However, intensive use of these insecticides have resulted a comprehensive pollution of the banana producing area of these islands. In order to control the toxicity of these pesticides, drinking water production plants were equipped with commercial activated carbon (AC) filters.

Plasma is a well-known fourth state of matter and is being used exclusively as a surface modifier and surface cleaning technique of polymers, powders, nanoparticles and so on for the past decade or more. In this research, cold plasma has been used to modify the surface of activated carbon in order to study the influence of new chemical species at its surface for adsorption of organic chlorinated compounds. Several characterization techniques for instance N2 adsorption desorption, X-ray photoelectron spectroscopy, scanning electron microscope etc. were further used to investigate the surface chemistry of plasma treated activated carbon.

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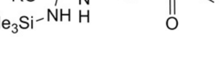
Inorganic and Coordination Chemistry **IC52**

Phosphorus, Nitrogen and Silicon-containing Acrylate Ester compounds as Flame Retardant Materials

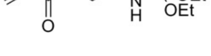
Jia En Low , Joëlle Levalois-Grützmacher

ETH Zürich, Wolfgang-Pauli-Strasse 10, 8093 Zürich, Switzerland

Phosphoramidates are a class of organophosphorus compounds showing promising potential for this purpose because of ease of their synthesis and their efficient flame retardant properties. It has been previously shown that, through the plasma-induced graft polymerization (PIGP) technique, flame retardant properties could be conferred onto the fabrics by modifying the surface of cellulose using acrylate monomers containing phosphoramidate (P-N) bonds [1]. As the synergistic effect of silicon as flame retardants has been investigated in the literature [2], our objective is to incorporate silicon into the acrylate monomers as flame retardants, combining the synergistic effects of all these three elements (P, N, Si)[3]. These effects are applied onto cellulose-based textiles via the PIGP technique. The flame retardant properties of these new compounds are then compared with those of the phosphoramidate systems.



Phosphorosilylamidates
(R= Me, Et, Ph)



Diethyl(acryloyloxy)ethylphosphoramidate

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Inorganic and Coordination Chemistry **IC53**

Direct Observation of Reaction Intermediates in Heterogeneous Alkene Metathesis Catalysts by NMR spectroscopy

Victor Mougel, Matthew P. Conley, Maxence Valla, Christophe Copéret*

ETH Zürich, Department of Chemistry, Laboratory of Inorganic Chemistry,
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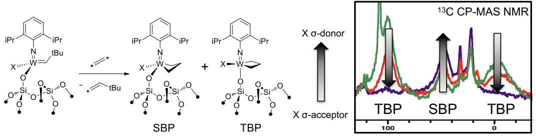
Advances in homogeneous olefin metathesis catalysts in the last 30 years have transformed the way in which a large number of organic molecules are prepared; alkene metathesis is widely used, from large scale conversion of ethene/butene into propene to the synthesis of fine chemicals. Despite major advances, understanding of active sites and reaction intermediates remain poor in heterogeneous catalysis.[1]

Here, using well-defined silica supported W-based catalysts, ≡SiOW(=NAr)(=CHR)(X), two catalytic intermediates are observed: they correspond to metallacyclobutanes with trigonal bipyramid (TBP) and square-based pyramid (SPY) geometries, whose TBP/SPY ratio decreases on going to more σ-donating X-ligands (Scheme 1).



Scheme 1.

In view of the direct relation between structures of metallacyclobutanes and catalytic performance (activity and stability),[2] observing them constitute an important step towards a molecular understanding of these systems.

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Inorganic and Coordination Chemistry **IC54**

Understanding metal ion binding ability, thermodynamic stability and structure of a metallothionein from *Musa acuminata* (banana)

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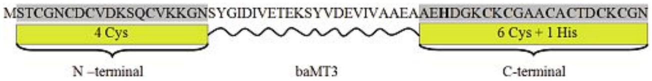
Metallothioneins (MT) are a ubiquitous class of proteins with an extremely high cysteine content, which have the ability to bind mono- and divalent metal ions with the electron configuration d^{10} in the form of metal-thiolate clusters. The metallothionein MT3 from *Musa acuminata* (banana) has been shown to bind 3 or 4 Zn(II) ions[1]. However, the apparent flexibility of the protein prevented any structural investigations.

We are studying the metal ion complexes of the N- and C-terminal Cys-rich domains of the protein in order to understand their metal ion binding abilities, structure and thermodynamic stabilities.

The combination of mass spectrometry as well as UV-Vis, CD, and NMR spectroscopy allows us to determine the amount of bound metal ions and to identify the metal ion binding sites in each domain, while potentiometric pH titrations enable the characterization of the thermodynamic stability of such metal-Cys-rich peptide complexes.



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Inorganic and Coordination Chemistry **IC55**

Metal complexes with N-heterocyclic carbenes bearing redox active groups

Ewa Milopolska, T. R. Ward*

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

In order to address some of the society's grand challenges, chemist's must master catalytic reactions involving multi-electron processes. In this context, redox active ligands offer an attractive means to tune the reactivity of transition metal complexes [1]. Thanks to its versatility in stabilizing transition metals in various oxidation states, we have selected the N-heterocyclic carbene as a scaffold, to which we append a variety of redox active moieties. We will present preliminary results summarizing our efforts in synthesizing and studying the coordination- and redox properties of such N-heterocyclic carbenes with a variety of transition metal complexes.

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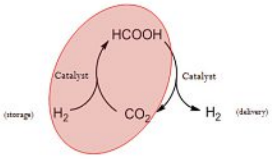
Inorganic and Coordination Chemistry **IC56**

Carbon dioxide for hydrogen storage

Séverine Moret, Paul J. Dyson, Gábor Laurenczy

Laboratory of Organometallic and Medicinal Chemistry/Ecole
polytechnique Féderale de Lausanne,BCH, 1015 Lausanne, Switzerland

Because of the increase in worldwide energy demand, renewable energy technologies are needed to reduce the dependence on fossil fuels and emission of greenhouse gases and other pollutants. Hydrogen has attracted growing attention as an energy carrier for both environmental and economic reasons. However, its storage remains a challenge: Conventional hydrogen storage methods, like high-pressure gas bottles and cryogenic liquid containers, have weight and safety issues. Formic acid can be used as a hydrogen carrier, for storage and delivery, via its catalytic decomposition into CO_2 and H_2[1-2]. To close the cycle of the system, the efficient hydrogenation of CO_2 is necessary[3-5].



Acknowledgements:
EOS holding and EPFL are thanked for financial support

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Inorganic and Coordination Chemistry **IC57**

The Effect of Sulfur-Functionalised Cyclometallating Ligands on the Photophysical Properties of Iridium(III) Complexes

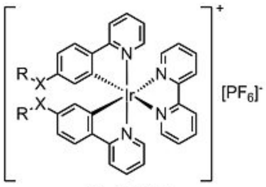
Cathrin D. Ertl, Edwin C. Constable, Catherine E. Housecroft

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

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

New cyclometallating ligands containing a variety of alkyl substituted thioether and sulfone functional groups in the 4-position of the phenyl ring have been synthesised. Heteroleptic Ir(III) complexes of these ligands (Figure 1) have been prepared in order to investigate the influence of the sulfur substituents on the photophysical properties of the complexes.

Interestingly, the sulfonyl substituents exert a relatively large blue-shifting effect when compared to the fluoro-substituted analogue. If the new complexes prove to be stable under LEEC conditions, sulfone functional groups will become promising alternatives to fluorine substituents in the pursuit of stable and efficient green/blue emitters based on cyclometallated Ir(III) complexes.



X = S, S(O)$_2$

Inorganic and Coordination Chemistry **IC58**

Peptide backbone B_{12} derivatives: Insights into His-on enzymatic processes

Marjorie Sonnay, Felix Zelder*

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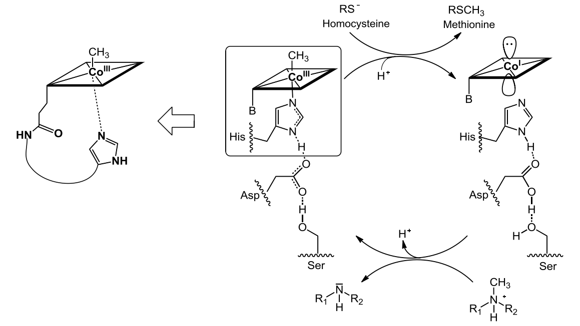
Vitamin B_{12} derivatives are used as cofactors by several enzymes, as methionine synthase or methylmalonyl CoA mutase.[1] Such proteins have the interesting ability to control the cofactor's stability and reactivity through a proton shuttle, which binds to the B_{12} derivative lower face via a histidine residue.[2] This so-called "base-off/His-on" binding mode thus appears as crucial for enzymatic processes. Hence, we propose to study this enzymatic cofactor activation, using a backbone modified B_{12} derivative as biomimetic model. In this derivative, the original backbone of vitamin B_{12} is replaced by a peptide loop terminated with an imidazole base.[3]



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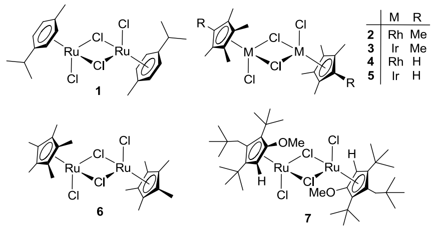
Inorganic and Coordination Chemistry **IC59**

Efficient and Rapid Synthesis of Chloro-Bridged Halfsandwich Complexes of Ruthenium, Rhodium and Iridium by Microwave Heating

Justus Tönnemann

EFPL, ISIC, LCS, 1015 Lausanne

The dinuclear complexes [(*p*-cymene)RuCl$_2$]$_2$ and [(cyclopentadienyl)MCl$_2$]$_2$ (M = Ru, Rh, Ir) are important starting materials with applications ranging from medicinal to supramolecular chemistry. The standard synthesis of these complexes involves heating an alcoholic solution of Ru^{III}, Rh^{III}, or Ir^{III} salts with precursors of the π-ligands for several hours under reflux. We found that microwave heating allows to obtain these complexes within few minutes without compromising the yields.



	M	R
2	Rh	Me
3	Ir	Me
4	Rh	H
5	Ir	H

The new synthetic procedures are advantageous because they involve a lower amount of solvent and, in some cases, of ligand precursor. Importantly, the reaction times can be shortened substantially from several hours to a few minutes.

Inorganic and Coordination Chemistry **IC60**

Anion Effects in Ru/PNNP-Catalyzed Asymmetric Imine Aziridination

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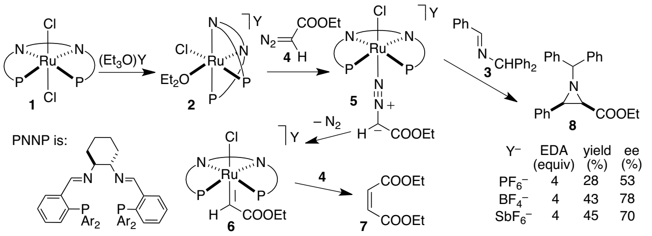
Our group has recently reported[1] that [RuCl(OEt$_2$)(PNNP)]PF$_6$ (**2**) catalyzes the asymmetric aziridination of imine **3** with ethyl diazoacetate (**4**) with the intermediacy of the diazoester complex **5**. This complex either transfers carbene to the imine or decomposes to the carbene complex **6**, whose reaction with **4** gives diethyl maleate (**7**) and lowers the yield of aziridine **8**.



Y⁻	EDA (equiv)	yield (%)	ee (%)
PF$_6^-$	4	28	53
BF$_4^-$	4	43	78
SbF$_6^-$	4	45	70

Ligands such as water or diethyl ether are necessary to improve the aziridine yield,[1] probably because they slow down the decomposition of the diazoester complex **5** to **6**. As it is known that fluorinated anions may weakly coordinate to 16-electron complexes,[2] we decided to study the anion effects by using (Et$_3$O)Y (Y = PF$_6$, BF$_4$, or SbF$_6$) in the activation of precatalyst **1**. We find now that the nature of the anion affects the yield of aziridine with little impact on the enantioselectivity. Tetrafluoroborate as counterion gives the best compromise with 45% yield and 78% ee. Multinuclear NMR spectroscopic studies aimed at understanding this anion effect will be presented.

[1] M. Ranocchiari, A. Mezzetti, *Organometallics*, **2009**, *28*, 3611.
[2] W. Beck, K. Sünkel, *Chem. Rev.*, **1988**, *88*, 1405.

Inorganic and Coordination Chemistry **IC61**

Cycloadditions and Coordination of an Ester Functionalized 1,2,4-Oxadiphosphole

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Phosphorus heterocycles are important building blocks and versatile ligand systems for organometallic chemistry [1]. We synthesized the 1,2,4-oxadiphosphole (**1**) in high yield. It is the ester functionalized analog of the one published by Regitz in 1999 [2]. Compound (**1**) shows high potential for cycloadditions and it was possible to coordinate it to a tungsten precursor. The results will be presented on the poster.

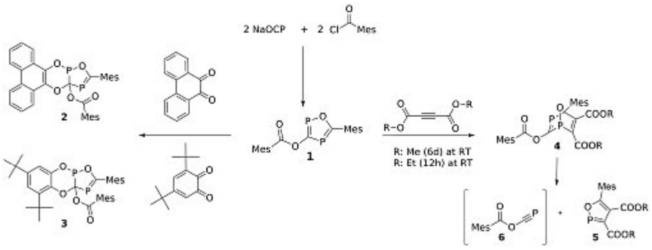

Figure 1: Cycloadditions of 1 with 1,2-quinones and activated acetylene.

[1] A. J. Arduengo, C. A. Stewart, *Chem. Rev.*, **1994,** *94*, 1215-1237

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Inorganic and Coordination Chemistry **IC62**

Molybdenum/Tungsten-Oxide Nanomaterials for Ammonia Sensing

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Molybdenum oxide has attracted much research attention due to its versatile structural chemistry in combination with interesting electronic properties and flexible chemical redox activity. Among the various molybdenum oxide structure types, metastable hexagonal molybdenum trioxide (h-MoO_3) excels through its unique tunnel motif, which gives rise to flexible intercalation chemistry together with interesting electrochemical and catalytic properties. This channel formation is often promoted by incorporation of alkali or alkaline earth guest cations so that ternary hexagonal molybdenum oxides with enhanced electronic, catalytic and surface properties are formed. We have studied the hydrothermal growth processes of structurally related W/Mo-nanomaterials in detail.[1] In our previous work, the ammonia sensing properties of alkali-containing hexagonal W/Mo-oxides indicated promising sensing performance.[2] In the next step, alkali-containing h-MoO_3 nanorods were investigated for their gas sensing performance. Starting from a hydrothermal approach, their particle size and surface-area-to-volume ratio were optimized for ammonia sensing applications. Optimization guidelines for the detection of reducing gases will be presented. The underlying mechanisms of interaction between oxide surface and test gas are still under investigation.

[1] Y. Zhou, N. Pienack, W. Bensch, G. R. Patzke, *Small* **2009**, 17, 1978-1983.

[2] Y. Zhou, K. B. Zheng, J.-D. Grunwaldt, T. Fox, L. L. Gu, X. L. Mo, G. R. Chen, G. R. Patzke, *J. Phys. Chem. C* **2011**, 115, 1134-1142.

IC63

Nitrogen-substituted, chiral (phenylethyl)-ferrocenes in catalysis

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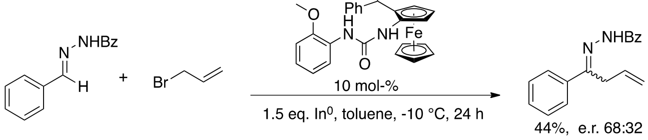
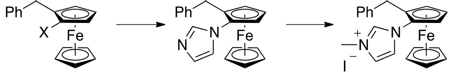
A series of nitrogen-substituted ferrocenes with a chiral aromatic backbone were prepared starting from Ugi's amine [1]. It could be shown, that ferrocenyl-ureas catalyse allylic substitutions with remarkable enantioselectivity [2].



This result was motivation to prepare other ferrocenes, tryting to further exploit the remote influence of the chiral center, or bringing it closer to the reaction center.

2-(Phenylethyl)-ferrocenylimidazole was prepared in moderate yield *via* Ullmann coupling. This is one of the rare examples of *ortho* – substituted ferrocenyl imidazoles and the first one to be prepared *via* Ullmann coupling. Substitution with an alkyl halide gives the respective imidazolium salt, which can be used as a ligand for various metals and catalytic purposes.



[1] G. W. Gokel, I. K. Ugi, *J. Chem. Educ.* **1972**, *49*, 294

[2] R. Aardoom, Monopnictogen Ferrocenes as Ligands for Asymmetric Catalysis. Diss. ETH No. 20635, ETH Zurich, **2012**

Inorganic and Coordination Chemistry **IC64**

Polypyridyl ligands: a route to a large variety of self-assembled species

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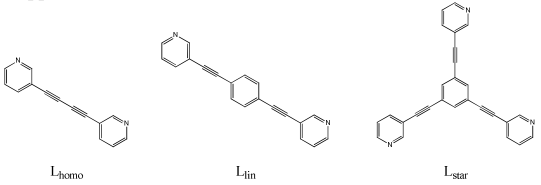
The use of pyridine as an N-donor ligand is extremely widespread. Because of the possibility of substituting the pyridine ring with different functional groups in multiple positions, various elaborated ligands can be obtained. The range of possibilities then provide various self-assemblies, depending on the nature of the metal center, stoichiometric ratios or the presence of other complexing groups. This work will present the use of three polypyridyl ligands (L_{homo},[1] L_{lin},[1] L_{star}[2]) of different size and symmetries. NMR titrations with silver(I) show the formation of finite species with stoichiometric ratios in good agreement with the formation of tetrahedrons (involving a planar trigonal coordination of the metal center). By changing silver for rhodium(II) paddle-wheel type complexes,[3] it should be possible to form species of different geometries such as triangles or octahedrons with uncapped faces.



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[3] Tong, L. H.; Clifford S.; Gomila A.; Duval S.; Guénée L.; Williams A. F., *Chem. Commun.* **2012**, *48*, 9891-9893.

Inorganic and Coordination Chemistry **IC65**

The d^{10} route to dye-sensitized solar cells: Step-wise assembly of zinc(II) photosensitisers on TiO$_2$ surfaces

Nik Hostettler, Edwin C. Constable, Catherine E. Housecroft, Biljana Bozic-Weber

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A large amount of the world's energy demand is still satisfied by the combustion of fossil fuels. Commercially available alternatives like silicon solar cells are still very expensive. Low priced and powerful alternatives are dye sensitised solar cells (DSCs). Although the most efficient cells still contain quite expensive ruthenium dyes, our group recently showed that very simple and cheap zinc(II) based dyes can be used instead. Zinc(II) complexes are normally colourless, i.e. they do not absorb in the visible region. To overcome this problem our group introduced a chromophore into the ligand, which yields colourful zinc(II) complexes, that are usable in DSCs. We were able to show that simple substituted terpyridine units are suitable as ligands for this purpose. The ligands investigated were 4'-(4-RC$_6$H$_4$)-2,2':6',2''-terpyridines with different R substituents (R = NPh$_2$, N(Ph-4-OMe)$_2$, N(Ph-4-NPh$_2$)$_2$), which were synthesised using Hartwig-Buchwald couplings.

Furthermore we introduced a new method to attach the dye onto the semiconductor surface, which includes a step-wise assembly of the metal complex on the surface, which avoids the need to isolate the heteroleptic zinc(II) complexes [1].

The electronic absorption as well as the performance of the complexes in DSCs has been studied. Synthesis of ligands and complexes will be presented along with NMR exchange studies and IPCE measurements.

[1] B. Bozic-Weber, E. C. Constable, N. Hostettler, C. E. Housecroft, R. Schmitt, E. Schönhofer, *Chem. Commun.* **2012**, *48,* 5727.

Inorganic and Coordination Chemistry **IC66**

Copper(I) bis(bipyridine) based complexes for DSCs

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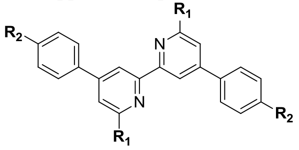
Since worldwide energy consumption is increasing, cheaper and more environmentally compatible energy production devices are needed. Dye-sensitised solar cells (DSCs) have the potential to fulfil these conditions. DSCs are built of a semiconductor covered glass plate functionalised with a dye. The broader the absorption range the better the photon harvesting from sunlight. The most efficient DSCs are based on ruthenium(II) dyes [1]. Due to the low natural abundance of ruthenium and its high price, alternative dyes for DSCs have to be found. As our group has shown in the past, copper(I) based dyes could be an alternative [2]. We are currently investigating new copper(I) complexes as alternative dyes for the application in DSCs.



R$_1$ = methyl, *n*-butyl, *sec*-butyl, hexyl, aryl.

R$_2$ = Br, *tert*-amine.

Derivatives of the 2,2'-bipyridine have been synthesized and used as ligands for the preparation of copper(I) dyes. The 2,2'-bipyridine derivatives have been modified in 4,4',6,6' position [3] in order to evaluate their influence on the performance in a DSC.

[1] Md. K. Nazeeruddin, M. Graetzel, et al., *J. Photochem. Photobio. A,* **2007**, *185*, 331-337.
[2] T. Bessho, E. C. Constable, M. Graetzel, A. Hernández Redondo, C. E. Housecroft, W. Kylberg, Md. K. Nazeeruddin, M. Neuburger, S. Schaffner, *Chem. Commun.*, **2008**, *32*, 3717-3719.
[3] D. Sakamaki, A. Ito, et al., *Angew. Chem.*, **2012**, *124*, 8406-8410.

Inorganic and Coordination Chemistry **IC67**

In Situ Monitoring of Copper Oxide and Copper Formation

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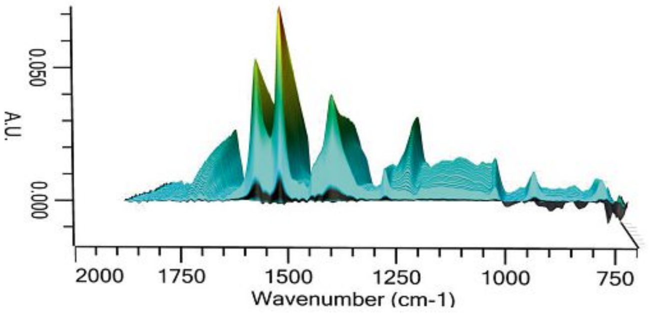
Formation of metal oxides by non-aqueous sol-gel method is an example of coupling organic and inorganic reactions. In situ monitoring of organic and inorganic species evolution during the reaction gives a possibility to elucidate the mechanism and the kinetics of the reaction.

Two spectroscopic techniques were applied to study the reaction between copper(II) acetylacetonate (precursor) and benzyl alcohol (solvent) at 140 °C and at 170 °C. Copper(I) oxide is a final inorganic product when the reaction is carried out at 140 °C. When the temperature increases then the Cu$_2$O particles are reduced and the final product is metallic copper. [1]

The organic species were followed by FTIR spectroscopy (see figure below) and the inorganic species were tracked by UV-VIS spectroscopy. Combination of these two techniques can be a powerful tool for in situ monitoring of non-aqueous sol-gel reactions.



[1] Niklaus Kränzlin, Stefan Ellenbroek, Desirée Durán-Martín, Markus Niederberger, *Angew. Chem. Int. Ed.* **2012**, 51, 4743 –4746.

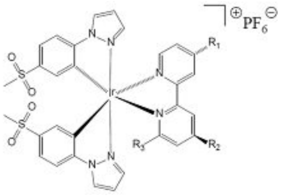
Inorganic and Coordination Chemistry **IC68**

Efficient Green Light-emitting Electrochemical Cells Based on a Sulfone Substituent on the Cyclometalating Ligands in an Iridium(III) Complex

A. M. Bünzli,[1] D. Tordera,[2] A. Pertegás,[2] J. M. Junquera-Hernández,[2] E. C. Constable,[1] J. A. Zampese,[1] C. E. Housecroft,[1] E. Ortí,[2] H. J. Bolink.[2]

[1]University of Basel, Spitalstrasse 51, CH-4056 Basel, Switzerland
[2]Instituto de Ciencia Molecular, Universidad de Valencia, 46980 Paterna, Spain

Light-emitting electrochemical cells (LECs) consisting of an iridium(III) based ionic transition metal complex (iTMC), sandwiched between two electrodes show promising properties for highly efficient and low-cost applications in ultra-thin flexible lighting. iTMCs support all the required processes of charge injection, charge transport, emissive recombination and can be deposited by spin coating casts.



1 R$_1$ = R$_2$ = R$_3$ = H
2 R$_1$ = R$_2$ = ^{t}Bu, R$_3$ =H
3 R$_1$ = R$_2$ = SMe, R$_3$ =H
4 R$_1$ = R$_2$ = NMe$_2$, R$_3$ = H
5 R$_1$ = R$_2$ = ^{t}Bu, R$_3$ = Ph
6 R$_1$ = H, R$_2$ = SMe, R$_3$ = Ph

Herein we present a series of very efficient green-emitting LECs with high luminance levels in simple LEC devices [1]. A new synthetic approach of obtaining green-emitting iridium(III) complexes based on a sulfone substituent on the phenylpyrazole cyclometalating ligand is shown as well as their photo- and electrophysical properties supported with the help of density functional theory calculations.

[1] D. Tordera, A. M. Bünzli, A. Pertegás, J. M. Junquera-Hernández, E. C. Constable, J. A. Zampese, C. E. Housecroft, E. Ortí, H. J. Bolink, *Chem. Eur. J.* (**2013**) in press

Inorganic and Coordination Chemistry **IC69**

Photoinduced charge transfer through metal-modified nucleic acids: Towards molecular wires.

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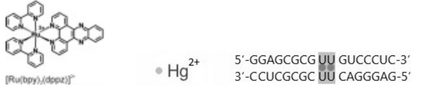
The application of nucleic acids as building blocks to generate molecular wires would vastly benefit from their superb self-assembly capacity and well-defined structural features. Unfortunately, the conductivity of natural nucleic acids is insufficient for their direct application in nano-scale electronic architectures. Site specific functionalization of nucleic acids with metal ions can overcome this shortcoming.[1,2]

Our goal is to investigate the electronic properties of metal-modified nucleic acids by photoinduced charge-transfer experiments using metallo-intercalators. These would act as electron donor-acceptor couple binding to metal-modified RNA sequences at specific sites. Our RNA sequences contain uracil-uracil miss-matched base pairs that coordinate Hg^{II} ions forming U-Hg-U base pairs.[3] Using absorption and emission experiments, we characterize the binding of the donor metallointercalator $[Ru(bpy)_2(dppz)]^{2+}$ into our RNA duplexes to reveal exact binding constants. Our recent studies suggest an intercalative binding mode between the light-switch complex and our Hg^{II} modified RNA duplexes.



Financial support by the Swiss National Science Foundation, the University of Zurich, within the COST Action CM1105 is gratefully acknowledged.

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[3] S. Johannsen; S. Paulus; N. Düpre; J. Müller; R. K. O. Sigel, *J. Inorg. Biochem.* **2008,** 102, 1141-1151.

Inorganic and Coordination Chemistry **IC70**

Binary Superlattices from Colloidal Nanocrystals and Giant Polyoxometalate Clusters

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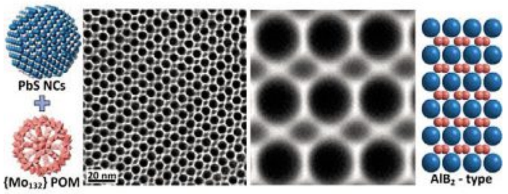
EMPA − Swiss Federal Laboratories for Materials Science and Technology, CH-8600 Dubendorf, Switzerland

We present a novel kind of long-range ordered binary superlattices comprising atomically defined inorganic clusters and colloidally synthesized nanocrystals.[1] As a proof-of-the-concept, we combined surfactant-encapsulated, nearly spherical giant polyoxometalate clusters containing 2.9 nm polyoxomolybdate or 2.5 nm polyoxovanadomolybdate cores with monodisperse colloidal semiconductor nanocrystals (PbS, CdSe, PbS/CdS; 4−11 nm). The obtained structures are rationalized on the basis of entropy driven crystallization of sterically stabilized colloidal. In particular, we obtained known thermodynamically stable binary packings of hard-spheres such as NaCl, AlB_2, and $NaZn_{13}$ lattices and also $CaCu_5$-type lattice and aperiodic quasicrystals with 12-fold symmetry. Following same strategy, we expect that work other kinds of cluster materials such as fullerenes can be integrated into supramolecular assemblies with nanocrystals.



[1] M. I. Bodnarchuk, R. Erni, F. Krumeich, M. V. Kovalenko, *Nano Lett.*, **2013**, *13*, 1699

Inorganic and Coordination Chemistry **IC71**

A controlled surface approach to generate ultrabright silica nanoparticles for bioimaging.

Giuseppe Lapadula,[1] Adrien Bourdolle,[2] Florian Allouche,[1] Matthew Conley,[1] Christophe Copéret,[1] Olivier Maury[2] Richard A. Andersen.[6]

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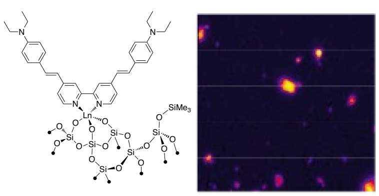
2 Université de Lyon, Ecole Normale Supérieure de Lyon, France
3 Department of Chemistry, University of California, Berkeley, CA 94720, USA

Bio-imaging requires ultrabright luminescent molecules or objects, whose emission falls in the biological window ($600<\lambda<1100$nm). We recently showed that controlled surface chemistry on 12-nm silica nanoparticles allows the installation of 200 well-defined chromophores at their surface.[1] Here, we show the development of Lanthanide-based systems, which readily absorbs two photon and emits sharp emission bands in the near IR, thus making them compatible with bio-imaging.[2]

Here, we will discuss the development of lanthanides functionalized silica nanoparticles and their molecular analogues with a molecular level understanding of the physical properties of the nano-objects.



1 Rendon, N.; Bourdolle, A.; Baldeck, P. L.; Le Bozec, H.; Andraud, C.; Brasselet, S.; Copèret, C.; Maury, O. *Chem. Mater.* **2011**, *23*, 3228.

2 Yuste, R. *Nat. Methods* **2005**, *2*, 902. (b) Campagnola, P. J.; Loew, L. M. *Nat Biotechnol.* **2003**, *21*, 1356.

Inorganic and Coordination Chemistry **IC72**

A highly efficient chromophore to generate ultra-bright silica nanoparticles via surface organometallic chemistry approach.

Giuseppe Lapadula[a] Shi Xia Liu[b], Olivier Maury,[c] Christophe Copéret[a], Silvio Decurtis.[b]

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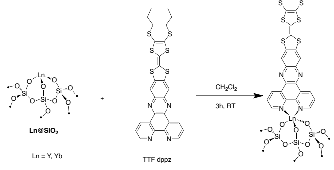
[b] *Universität Bern, Freiestrasse 3, 3012 Bern*
[c] *Université de Lyon, 946 allée d'Italie, 69007 Lyon, France*

Surface organometallic chemistry allows generating ultra-bright silica nanoparticles which can hold more than 200 chromophores per 12-nm silica nanoparticle[1]. Using surface chemistry approach it is possible to incorporate a lanthanide ion (sharp emission in the near IR, long living excited states, low toxicity) into the surface and enhancing its emission properties through an antenna ligand, making them ideal candidates for microscopy in medical and biological applications. In this work, we focus on the preparation and the characterization of lanthanides doped silica nanoparticles and the grafting of a highly efficient chromophore (**TTF dppz**)[2] via surface organometallic chemistry



1 Rendon, N.; Bourdolle, A.; Baldeck, P. L.; Le Bozec, H.; Andraud, C.; Brasselet, S.; Copéret, C.; Maury, O. *Chem. Mater.* **2011**, *23*, 3228.

2 Jia C., Liu S., Tanner C., Leiggener C., Neels A., Sanguinet L., Levillain E., Leutwyler S., Hauser A., and Decurtins S. *Chem. Eur. J.* **2007**, *13, 3804 – 3812*