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Tailored Lanthanide Optical Probes

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A series of over 75 emissive lanthanide(III) complexes has been prepared designed to report on the local environment by modulation of spectral form, lifetime or circular polarisation [1][2]. These responsive complexes have been used for the *in vitro* analysis of key bioactive species (pH, pO_2, pX) in various biological fluids and for microscopy applications in viable living cells [3]. A key aspect has been the application of ratiometric methods, analysing the relative intensity of emission spectral bands for europium complexes, or examining both Eu and Tb emission in complexes of a common ligand [4][5].

The emission spectral form of Eu(III) complexes is sensitive to changes in the local coordination environment, arising from reversible coordination of certain anions to the metal centre. Complexes have been defined that can signal changes in bicarbonate, lactate and citrate based on this approach [3]. For example, citrate analyses of less than 1 L samples of prostate fluid have been made, seeking to correlate the reduction in citrate concentration with progression of prostate adenocarcinoma.

[1] C. P. Montgomery, B. S. Murray, E. J. New, R. Pal. D. Parker, *Acc.Chem.Res.* **2009**, doi: 10.1021/ar800174z.
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[3] R. Pal, D. Parker, L. C. Costello, *Org. Biomol. Chem.* **2009**, *7*, 1525
[4] E. J. New, D. Parker, *Org. Biomol. Chem.* **2009**, *7*, 851.
[5] E. J. New, D. Parker, R. D. Peacock, *Dalton Trans.* **2009**, 672.

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Excitation and Sequestration of the Lanthanides, a Coordination Chemistry Challenge [1]

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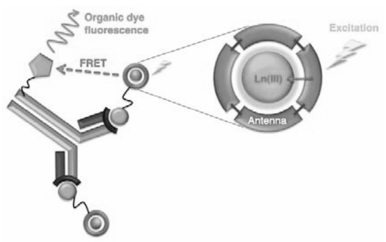
An overview of the coordination chemistry of the trivalent lanthanides will be given as background for the design and development of highly luminescent Ln(III) complexes (with Ln = Tb, Eu) for applications in biotechnology. In particular, developments utilizing the 2-hydroxyisophthalamide (IAM) chelate for Tb(III) and the 1 hydroxypyridin-2-one (1,2 HOPO) chelate for Eu(III) will be presented. A focus of our research has been the optimization of these compounds as potential commercial agents for use in Homogeneous Time Resolved Fluorescence (HTRF) technology, as illustrated by the figure at right. These assays have become widespread in pharmacology and biotechnology. By using the long-lived luminescence of a lanthanide energy donor, the sensitivity of this assay format can be vastly improved by using time gated excitation and detection. The fundamental chemistry behind this technology will be presented.



[1] Dedicated with respect and affection to Professor Jean-Claude Bünzli.

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Enlightening Science and Technology with Lanthanide Luminescence

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Lanthanides and light have been an un-dissociable couple for the past two centuries, much as Orpheus and Eurydice in their difficult search for each other. All of trivalent lanthanide ions, barring La^{III} and Lu^{III}, are luminescent and their emission is characterized by two decisive factors, sharp lines and long excited state lifetimes [1]. Provided the disadvantage of the low dipole oscillator strengths of f-f transitions is overcome by a sensitization process involving energy transfer from the surroundings, these two aspects make Ln^{III} ions inescapable when it comes to highly sensitive luminescent biosensing and bio-imaging [2]. Other applications range from agriculture to telecommunications, electroluminescent displays, and lightening devices.
The search for luminescent lanthanide-based molecular probes is exemplified for near-infrared- [3] and visible-emitting complexes [4]. Both the chelate effect and self-assembly processes are used to produce the required coordination environment around the Ln^{III} ion for maximum luminescence sensitization and protection against de-activation processes. Applications to luminescent liquid crystals, ionic liquids, live cell imaging [5] and detection of cancerous tissues are described.

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[3] J.-C. G. Bünzli, C. Piguet, *Chem Soc Rev.* **2005**, *34*, 1048.
[3] S. Comby, J.-C. G. Bünzli in *Handbook on the Physics and Chemistry of Rare Earths*, K. A. Gschneidner Jr., J.-C. G. Bünzli, V. Pecharsky, eds, Elsevier Science B.V.:Amsterdam **2007**, Vol. 37, Ch. 235.
[4] B. Song, C. D. B. Vandevyver, A.-S. Chauvin, J.-C. G. Bünzli, *Org. Biomol. Chem.* **2008**, *6*, 4125.

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Iron Carbonyl Pyridonate Complexes Related to the Active Site of the [Fe]-Hydrogenase (Hmd)

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The [Fe]-hydrogenase (Hmd), can catalyze the reversible reduction of methenyl-tetrahydromethanopterin (methenyl-H_4MPT^+) with H_2 to form methylene-tetrahydromethanopterin (methylene-H_4MPT) and H^+ (Figure 1).[1]

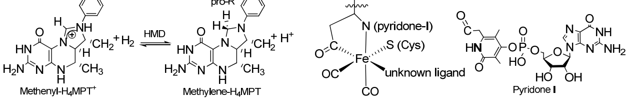

Figure 1. Function and structure of [Fe]-hydrogenase (HMD).

Here we present some monomeric iron bis(carbonyl) pyridonate complexes that are close mimics for the active site of [Fe]-hydrogenase (Figure 2). Complexes **2**-**4** contain all four essential Fe-coordinating ligands in the enzyme: two COs, one sulfur ligand, and one pyridone.

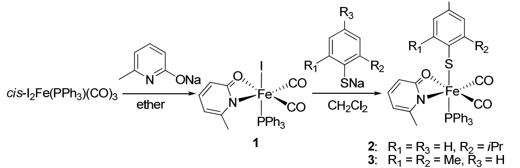

Figure 2. Synthesis of Fe pyridonate complexes.

[1] S. Shima, O. Pilak, S. Vogt, M. Schick, M. S. Stagni, W. Meyer-Klaucke, E. Warkentin, R. K. Thauer, U. Ermler, *Science* **2008**, *321*, 572-575.
[2] This work is supported by the EPFL and the Swiss National Science Foundation (project no. 119663).

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Nano-structured Ag-compounds as antimicrobial coatings

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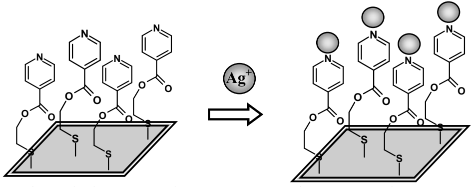
Over the last years, the interest in silver compounds and nanoparticles has been increasing due to their antimicrobial properties. In our group, we are working with silver coordination polymer networks as coating material for implant metal surfaces.[1,2]



We analyzed the coated surfaces, and present the nano-structured surface topography, the chemical composition of the coating on Au(111) as a model surface, the antimicrobial properties of the coated implants, and, on a molecular level, the interaction of silver ions with peptide sequences and subsequent silver nanoparticle formation.[3,4]

[1] A.Y.Robin, J.L.Sague Doimeadios, K.M.Fromm, *Cryst.Eng.Comm.*, **2006**, *8*, 403

[2] A. Y.Robin, J. L. Sague Doimeadios, A. Neels, T. Vig Slenters, K. M. Fromm, *Inorg.Chim.Act.*, **2007**, *360*, 212

[3] T.Vig Slenters, I.Hauser-Gerspach, A.U.Daniels, K.M.Fromm, *J.Mater.Chem.*, **2008**,*18*, 5359

[4] K.Belser, T.Vig Slenters, C.Pfumbidzai, G.Upert, L.Mirolo, K.M.Fromm, H.Wennemers, *Angew. Chem. Int. Ed.*, **2009**, *48*

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Fluorescence Sensors for Lithium Ions or Small Peptides in Water and Serum

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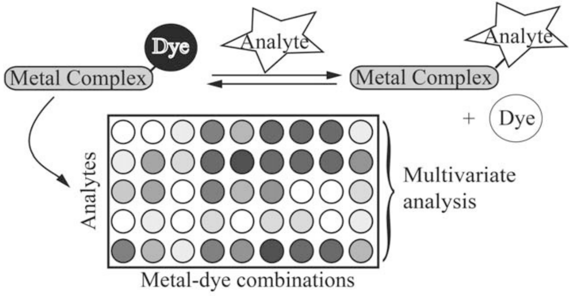
Selective detection of analytes in biological fluids such as serum represents a challenging task, considering the high complexity of these environments. Two approaches are presented here: a) the quantification of the biologically important lithium ion by a highly selective sensor; b) the detection and discrimination of small peptides by an indicator displacement assay.

Macrocyclic receptors, which are water-soluble and selective for lithium ions, have been developed in our laboratory. When a fluorescent dye is attached to them, they can be used to determine the lithium concentration in a serum-containing aqueous solution by a simple fluorescence measurement.[1]

Transition metals (Ru, Rh, Pd) were used together with selected fluorescent dyes to build a sensor array. Small peptides were efficiently differentiated and quantified using fluorescence spectroscopy in combination with multivariate analysis (figure).



[1] S. Rochat, Z. Grote, K. Severin, *Org. Biomol. Chem.* **2009**, *7*, 1147.

135

Ru(II)arene complexes as versatile antitumour agents

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Ruthenium half-sandwich compounds are attractive antitumour agents due to several features; low general toxicity of ruthenium, lipophilicity of the arene ligand leading to improved uptake into the cell, a wide range of possible ligands. One series of ruthenium(II)-arene-pta (RAPTA; pta = 1,3,5-triaza-7-phophaadamantane) compounds have been found to show particularly high selectivity towards tumour cells in both in vitro and in vivo studies.[1] By modifying the ligands around the ruthenium centre, we are able to improve desirable properties of the drugs such as increased lipophilicity or hydrophilicity, improved kinetic stability and reduced damage of healthy tissue.

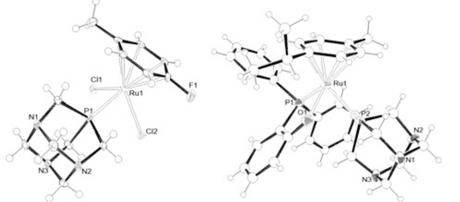

Figure 1: Examples of modified RAPTA compounds

[1] C. Scolaro, A. Bergamo, L. Brescacin, R. Delfino, M. Cocchietto, G. Laurenczy, T. J. Geldbach, G. Sava, P. J. Dyson, *J. Med. Chem.* **2005,** *48*, 4161-4171.

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Synthesis of high valent $[^{99m}TcO_3]^+$ complexes and [3+2] cycloaddition reactions with alkenes in water as a novel direct labeling strategy

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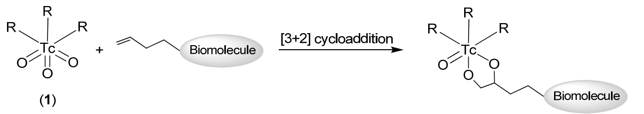
The labelling of small biomolecules with ^{99m}Tc under retention of bioactivity is the major challenge in modern radiopharmacy. To achieve this aim we developed a new labeling strategy using small technetium complexes containing the $[^{99m}TcO_3]^+$-core, which react with alkenes by a [3+2] cycloaddition.[1]



To establish this new approach as an alternative to today`s used labeling techniques, a fast and efficient synthesis of the $[^{99m}TcO_3]^+$ complex (**1**) at ambient temperatures is essential.

We report about a new synthetic pathway for the synthesis of $[^{99m}TcO_3(\text{tacn-R'})]^+$ (tacn = 1,4,7-triazacyclononane, R' = H, CH_2Ph) complexes by a sequential reduction-oxidation reaction starting from $[^{99m}TcO_4]^-$ in water. The reaction of $[TcO_4]^-$ with $NaBH_4$ at temperatures below 40°C leads to $[^{99m}TcO_3]$ complexes with high radiopharmaceutical purity in less than 30 minutes. Furthermore, first model reactions for the labeling of biomolecules via the [3+2] cycloaddition will be presented.

[1] H. Braband, Y. Tooyama, T. Fox, R. Alberto, *Chem. Eur. J.* **2009**, *15*, 633-638.

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Tailoring Spin Crossover in Solution Through Molecular Recognition Sites

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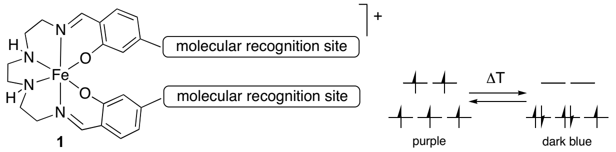
Spin-crossover complexes that show bistability and thermal hysteresis have attracted considerable attention for the fabrication of optical and magnetic memory devices [1]. Upon applying an external stimulus, eg. a temperature or a pressure gradient, SCO complexes undergo a change in magnetic moment. Such a switching process is strongly dependent on the molecular environment and on intermolecular contacts between the spin-labile metal centers. Hence, self-assembly techniques may be an attractive tool to induce an intermolecular arrangement that promotes strong cooperativity [2].



We recently reported that self-assembly of amphiphilic complexes of type **1** increases the spin transition temperature and makes the SCO event in solution significantly more abrupt [3]. We will discuss these effects and will show that modification of the molecular recognition sites allows for preparing systems that switch near RT and exhibit hysteresis.

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[3] C. Gandolfi, C. Moitzi, P. Schurtenberger, G.G. Morgan, M. Albrecht, J. *Am. Chem. Soc.* **2008**, *130*, 14434.

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Olefin Cross-Metathesis on Gold

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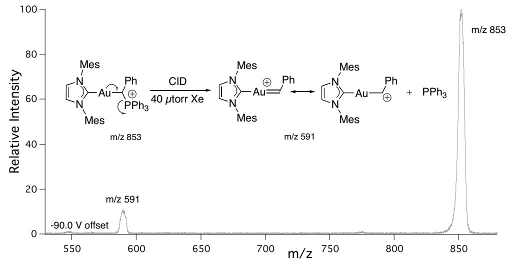
Gold carbenes and carbenoids are widely employed to rationalize outcomes of gold-mediated catalytic transformations [1]. We have developed a method for preparing those elusive species directly inside the mass-spectrometer [2].



Gas-phase reactivity studies led to the discovery of an olefin cross-metathesis manifold observed with 1,2-*cis*-dimethoxyethylene together with expectable cyclopropanation reactivity [2]. Mechanistic studies demonstrate that those channels do not share the same rate-determining transition state [3].

[1] A. Fürstner, and P. W. Davies, *Angew. Chem., Int. Ed.*, **2007**, *46*, 3410.
[2] A. Fedorov, M.-E. Moret, and P. Chen, *J. Am. Chem. Soc.* **2008**, *130*, 8880.
[3] A. Fedorov, and P. Chen, *Organometallics,* **28**, 1278 (2009).

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Design and Properties of Polynuclear Ln(III) Complexes

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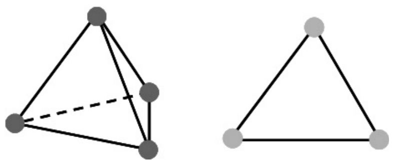
Good luminescent and paramagnetic properties of lanthanide complexes are crucial for sensing and imaging purposes in biomedical applications and significant effort is still devoted to their improvement. We are interested in a controlled preparation of discrete polymetallic arrays, which would provide an enhancement of signals by adding up contributions from all cations within a discrete supramolecular complex. Advantageously, different cations may be also combined in heterometallic systems allowing the development of multimodal probes and devices with boosted near-infrared emission.

Herein we present the self-assembly of three-dimensional tetrametallic helicates, where lanthanide cations adopt a tetrahedral arrangement.[1] The second part deals with trinuclear triangular complexes with a peculiar coordination mode.[2] X-ray crystal structures, solution properties and luminescence will be discussed in details for both systems.



[1] J. Hamacek, G. Bernardinelli, Y. Filinchuk, *Eur. J. Inorg. Chem.* **2008**, 3419-3422.
[2] S. Zebret, N. Dupont, G. Bernardinelli and J. Hamacek, *Chem. Eur. J.* **2009**, 15, 3355.

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Tuning of emission wavelength by modification of main ligand in Iridium complexes

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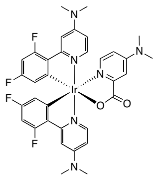
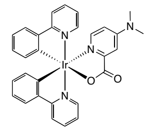
School of Basic Sciences, EPFL, CH-1015 Lausanne, Switzerland

Bis-cyclometallated iridium complexes are commonly used for dopants in OLEDs. They exhibit unique photophysical properties as full color tunability. This can be achieved by introducing various donor and acceptor group on the cyclometalated ligand. Due to HOMO and LUMO being localized mainly on different parts of the ligand, the color can be tuned in a predictable way.


N977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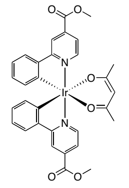
N958

This poster recal basic rules for color tuning and based on the **N958** example, we show that commonly used photophysical properties in solution are in fact poorly anticipating the device performances.[1]

[1] E. Baranoff, S. Suàrez, P. Bugnon, H. J. Bolink, C. Klein, R. Scopelliti, L. Zuppiroli, M. Graetzel, Md. K. Nazeeruddin, *ChemSusChem* **2009**, *2*, 305.

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The proximity of Pt in NO_x storage-reduction catalysts

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Automobile emission can be limited using NO_x storage reduction (NSR) catalysts typically containing $Pt/Ba/Al_2O_3$. Pt is essential for NO oxidation and NO_x reduction in such catalysts. Here, the effect of Pt proximity to the Ba storage sites was investigated on catalysts with preferential Pt location on Al or on Ba (Fig 1.) produced by a twin flame spray pyrolysis (FSP) unit. The spillover and support effect was elucidated by comparing $Pt/Ba/Al_2O_3$ with $Pt/Ba/CeO_2$. The best catalyst performance was found for materials with Pt near the Ba [1].

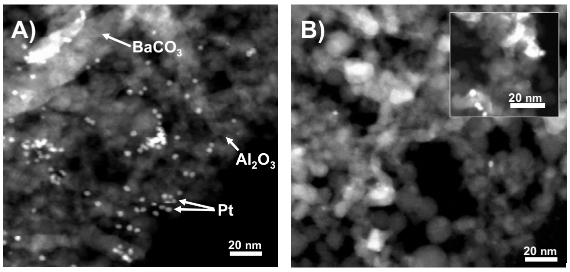

Figure 1: $Pt/Ba/Al_2O_3$ catalysts with Pt preferentially on Al_2O_3 in A) and Pt on $BaCO_3$ in B).

[1] R. Büchel, R. Strobel, F. Krumeich, A. Baiker, S. E. Pratsinis, J. Catal. **2009,** *261,* 201.

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Self-organized liquid-crystalline dendrimer-functionalized gold nanoparticles: a promising optical hybrid material

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Thomas Bürgi[3] and Robert Deschenaux[1]

[1]University of Neuchâtel, Institutes of Chemistry and Physics, rue Emile-Argand 11, CH-2009 Neuchâtel, Switzerland; [2]EPFL STI IMT-NE OPT, Institute of Microtechnology, rue A.-L. Breguet 2, CH-2000 Neuchâtel, Switzerland; [3]University of Heidelberg, Institute of Physical Chemistry, Im Neuenheimer Feld 253, DE-69120 Heidelberg, Germany

Our study focuses on the synthesis of well-defined gold nanoparticles (AuNPs) bearing liquid-crystalline (LC) dendrimer ligands in their shell, combining ligand exchange[1] and chemical ligand modification.[2]

Functionalization using thiolated dendrimers seems the easiest way to obtain these materials; however, large amounts of ligand are required in this case.[3] An alternative is the synthesis of tailored OH-functionalized AuNPs prior to the possible chemical reaction with the LC dendritic carboxylic acids.

These composites which self-organize[3] are promising candidates to build up artificial three-dimensional structures with unique properties (metamaterials).[4]

[1] A. Kassam, G. Bremner, B. Clark, G. Ulibarri, R. B. Lennox, *J. Am. Chem. Soc.* **2006**, *128*, 3476.
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[4] C. Rockstuhl, F. Lederer, C. Etrich, T. Pertsch, T. Scharf, *Phys. Rev. Lett.* **2007**, *99*, 017401.

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Xanthosine 5'-Monophosphate (XMP). Coordinating Properties of a Chameleon-like Nucleotide

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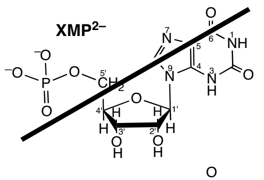
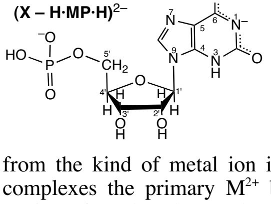
Xanthosine and its nucleotides are important metabolic intermediates and thus widely studied [1]. Unfortunately, the structure of the monophosphate commonly shown in textbooks depicts XMP^{2-} and this is not correct: (i) XMP^{2-} is a minority tautomer that occurs only to about 10%; the dominating one (90%) is $(X - H{\cdot}MP{\cdot}H)^{2-}$ which carries a proton at the phosphate group but has lost one from the (N1)H/(N3)H sites, thus giving rise to further ambiguities [2]. (ii) Most importantly, in the physiological pH range of about 7.5 XMP is present as the 3-fold *negatively* charged $(X - H{\cdot}MP)^{3-}$ species!



XMP^{2-}



$(X - H{\cdot}MP{\cdot}H)^{2-}$

The two most relevant complexes formed with divalent metal ions (M^{2+}) are $(M{\cdot}X - H{\cdot}MP{\cdot}H)^{\pm}$ and $(X - H{\cdot}MP{\cdot}M)^{-}$ [2]. In the first case M^{2+} is N7-coordinated, forming to about 65% outersphere macrochelates with the $P(O)_2(OH)^{-}$ group; note, the given formation degree is independent from the kind of metal ion involved. In contrast, in the $(X - H{\cdot}MP{\cdot}M)^{-}$ complexes the primary M^{2+} binding site is the PO_3^{2-} group and macrochelates form in this case innersphere with N7, the formation degree being strongly dependent on the kind of M^{2+} involved, e.g., being 0% with Mg^{2+}, 50% with Mn^{2+}, and 90% with Zn^{2+} [2].

Supported by the Department of Chemistry of the University of Basel.

[1] Review: E. Kulikowska, B. Kierdaszuk, and D. Shugar, *Acta Biochim. Polonica*, **2004**, *51*, 493–531.
[2] H. Sigel, B. P. Operschall, and R. Griesser, *Chem. Soc. Rev.* **2009**, *38*, in press.

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Synthesis of ditopic 2,2':6',2''-terpyridine ligands and their Fe(II) and Ru(II) complexes.

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The $\{M(tpy)_2\}^{n+}$ (tpy = 2,2':6',2"-terpyridine) motif is increasingly used in preference to $\{M(bpy)_3\}^{2+}$ (2,2'-bipyridine) domains in supramolecular chemistry.[1] One major reason is that $\{M(bpy)_3\}^{2+}$ is chiral and the incorporation of multiple centres gives rise to diastereoisomeric structures. This is not to say that $\{M(tpy)_2\}^{n+}$ motifs cannot be chiral; the commonest stereogenic factor is the desymmetrization of the ligand by substitution on one of the two terminal rings. We recently demonstrated that a symmetrical ligands linked through flexible chains can also give rise to chiral structures as a result of the "trapping" of the chain between tpy domains.[2]

We now describe the extension of these observations to new types of bis(2,2':6',2"-terpyridine) ligands and report the spectroscopic characterisation of atropisomeric complexes of these ligands and the investigation of the dynamic processes interconverting the enantiomers.

[1] Constable, E.C. *Chem. Soc. Rev.* **2007**, *36***,** 246-253.
[2] Chow, H.S.; Constable, E.C. and Housecroft, C.E. *Dalton Trans.* **2003**, 4568-4569.

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Gold(I) phosphine derivatives of 4,4'-dialkynyl substituted 2,2'-bipyridine

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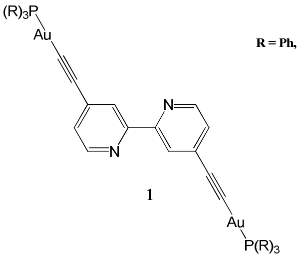
Gold(I) phosphine derivatives have the potential to be luminescent and have interesting optical properties [1].

Ligand **1** can be synthesized from 4,4'-dialkynyl substituted 2,2'-bipyridine and trialkyl- or triarylphosphine gold(I) chlorides. A series of these compounds have been structurally characterized, and the influence of changing the alkyl or aryl substituents on their structures and absorption and emissive properties will be discussed.



R = Ph, *p*-Tol, *t*-Bu, Et, *i*-Pr

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Anion and Solvent Effects on the Synthesis of Cobalt Complexes of Ditopic 2,2':6',2''-Terpyridine Ligands with Flexible Spacers

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The reaction of transition metal ions with ditopic ligands containing two 2,2':6',2''-terpyridine units linked by flexible spacers can give metallopolymers (copolymers with alternating metal centres and ligands), discrete molecular macrocycles, or mixtures of the two. The outcome of the coordination depends on the precise reaction conditions as well as the nature of the spacer and the transition metal salt.

We have used ditopic ligands with two 2,2':6',2''-terpyridine units linked by flexible oligo(ethyleneoxy) spacers to synthesise cobalt(II)-containing metallomacrocycles of various sizes. Their dynamic behaviour in solution has been studied using ^1H NMR spectroscopy. Oxidation of these products to give the cobalt(III) species has allowed us to investigate these compounds with diffusion NMR spectroscopy and thus to determine their relative sizes in solution.

We have isolated neutral mono-2,2':6',2''-terpyridine complexes with labile transition metal ions. The interplay between metallomacrocycles and polymers is strongly dependent on the counteranion and the solvent mixture, with the assembly of polymers favoured in the presence of coordinating anions and in non-coordinating solvents.

Increasing the reaction temperature and using pure methanol or ethanol as the solvent for the complexation resulted in the decomposition of the ditopic ligand and formation of a simple bis(4'-alkoxy-2,2':6',2''-terpyridine) cobalt(II) complex when cobalt(II) acetate was used as the source of cobalt. This reaction can be extended to allow interchange of alkoxy groups on monotopic 4'-alkoxy-2,2':6',2''-terpyridines.

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Encapsulation of Functionalised Pyrenyl Molecules in Hexanuclear Arene Ruthenium Cages

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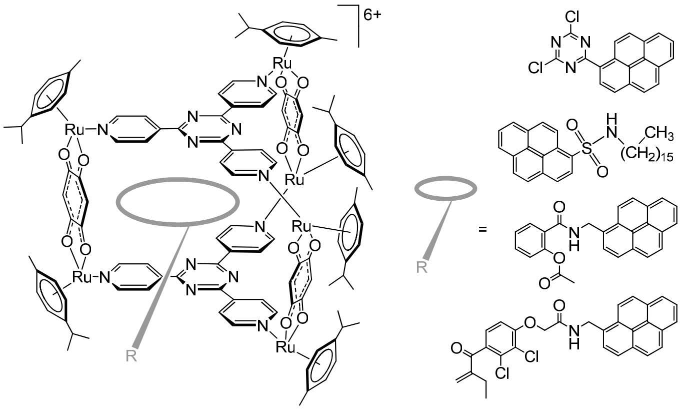
The cationic metalla-prism, $[Ru_6(p\text{-cymene})_6(tpt)_2(dhbq)_3]^{6+}$, incorporating *p*-cymene ruthenium units, bridged by dihydroxy-1,4-benzoquinonato (dhbq) ligands, and connected by 2,4,6-tris(pyridine-4-yl)-1,3,5-triazine (tpt) panels allow the encapsulation of large aromatic molecules [1].



This water soluble cage is now used to encapsulate various functionalised pyrenyl molecules in which the functional group is hanging out of the cage, while the pyrenyl part is encapsulated, thus providing a new approach for drug delivery.

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148

Ni-catalyzed Kumada-Corriu-Tamao coupling of Alkyl Grignard Reagents with Functionalized Aklyl halides

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The catalytic activity of the Ni^{II} pincer complex $[(^{Me}NN_2)Ni\text{-}Cl]$[1] complex in Kumada-Corriu-Tamao coupling of nonactivated Alkyl bromides and iodides was studied (Fig. 1)[2,3]. All experiments were carried out in DMA solvent at -35^{0}C, just above the freezing point of the mixture. The coupling is completed in 30 minutes and the product is easily separated and isolated. A wide array of primary Alkyl bromides and iodides as well as secondary Alkyl iodes could be coupled. Excellent group tolerance was found. Substrates with reactive groups as ester, ether, ketone, alcohol or heterocyclic compounds can be used in this reaction and coupling was selective for alkyl-Br and alkyl-I moieties. A range of alkyl Grignard reagents could be used.

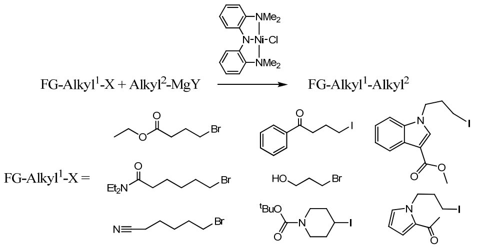

Figure 1. Ni-catalyzed coupling of nonactivated FG-Alkyl-Br,I.

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SYNTHESIS OF MOLECULAR NANOSTURUCTURES BY MULTICOMPONENT CONDENSATION REACTIONS IN A BALL MILL

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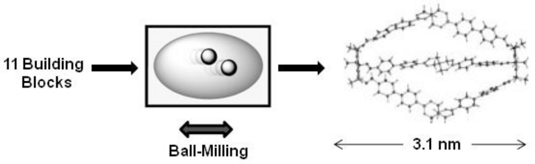
and K. Severin*

Institut des Sciences et Ingénierie Chimiques, Ecole Polytechnique Fédérale
de Lausanne (EPFL), CH-1015 Lausanne, Switzerland



Over the years, evidence has accumulated that a solvent-free synthesis promoted by grinding can be an interesting alternative to classical solution-based methods. Obvious benefits include the reduced economic and ecological costs when working without a solvent. In addition, a solvent-free synthesis may display an increased rate and yield and a better selectivity. Despite its success in organic synthesis, there are only a few reports about the utilization of grinding techniques for the construction of molecularly defined nanostructures.

We will describe the syntheses of two boron-based molecular cages, which were obtained by multicomponent condensation reactions in a ball mill.[1] The synthesis of these cages requires the formation of 18 covalent bonds between 11 building blocks. Crystallographic analyses show that the cages are among the largest boronic acid-based macrocyclic structure known to date. Evidence is provided that the solvent-free reactions are superior in terms of yield and purity.

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151

Polyether adducts of d-block metal compounds as starting materials for new cluster compounds.

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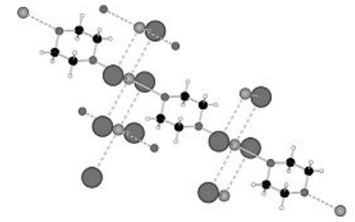
We are interested in molecular compounds, especially oxygen donor adducts of metal halides, because they are used as starting materials in the synthesis of low-dimensional polymeric compounds, i. e. clusters, and polymers or metal organic frameworks.[1-5] Indeed, since more than two decades, metal aggregates are used in the low-cost synthesis of superconductors and other oxide materials. However, the chemistry of such metal halide or pseudo-halide adducts with neutral Lewis-coordinating ligands is still not systematically studied. In this context, we have synthesized and characterized some new molecular compounds using polydentate neutral Lewis-coordinating ligands in order to understand better the chemistry of d-block metal halides in aprotic solvents. Secondly, we were interested in the study of the influence of the size of the ligand on the coordination sphere of the metal cation using monodentate or polydentate O-donor ligands.



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Multitopic Ligand Approach for the Synthesis of Oxidic Materials

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Mixed metal materials can be used in different applications, for instance in opto-electronic devices or as metal oxides in high-Tc superconductors (BSSCO, YBCO) [1, 2, 3]

A synthetic strategy to obtain mixed metal oxides is to use decomposition techniques like (metal-organic) chemical vapor deposition (MO-CVD) to combust metal-containing volatile complexes. Complexes of alkaline earth and group 11 metal ions may for example provide such precursors.

We developed a multitopic ligand system, where different metal ions can be successively coordinated. This way, it is possible to tailor the properties (e.g magnetic, opto-electronic) of the multimetallic compounds.

To obtain mixed metal oxides ($Ca_xCu_yO_z$ or $Ba_xCu_yO_z$), we use different methods like combustion/sintering of the compounds or also evaporation techniques like MO-CVD. The so obtained oxides are characterized by XRD, SEM and EDS.

We will show that this concept works by presenting the synthesis pathways and also by showing first results obtained for mixed metal oxides, which could be used for the synthesis of BSSCO or YBCO. [4]

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Cycloisomerization of 1,6-Enynes Catalyzed by an Iridium Phosphoramidite Complex

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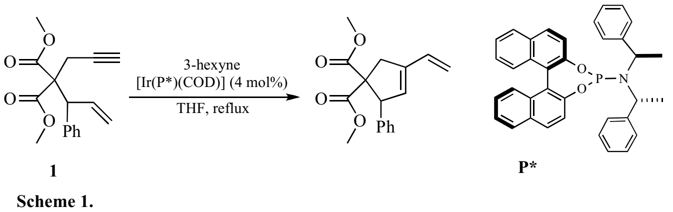
The catalyzed cycloisomerization of 1,6-enynes usually needs strong π-acceptor ligands such as carbon monoxide. Until now iridium-based catalysis proceeded only under a CO atmosphere [1].

We investigated the catalytic cycloisomerization of dimethyl (*R*)-2-(1-phenylallyl) propargylmalonate **1** according to Scheme 1 using 3-hexyne (3 eqiv) and [Ir(COD)(P*)]SbF_6 **2** as catalyst. The catalyst was activated by chloride abstraction from [IrCl(P*)(COD)] with $AgSbF_6$. Although the substrate had been completely consumed, the yield for the unsubstituted 1,6-enyne (45 %) was mediocre but similar to reports in the literature [1].

In sum, we discovered a new iridium-based catalyst for the cycloisomerization of 1,6-enynes that does not require the use of toxic carbon monoxide.



Scheme 1.

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Investigations of Lanthanides Complexes with Short Symmetrical Tripodal Ligands

Jingpeng Sa, Laure Guénée, Josef Hamacek*

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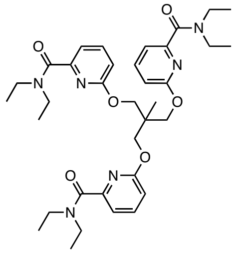
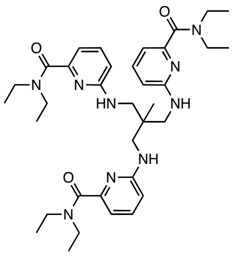
Recently, the short tripodal receptors have been designed for the preparation of three-dimensional tetrametallic helicates.[1] In this work, the multistep synthesis of two structurally similar symmetric tripodal ligands **L1** and **L2** has been prepared using a modified catalytic procedure.[2] The lanthanide complexation is achieved by the coordination units of the type 'O-N-O' or 'N-N-O', respectively. The reaction of **L1** with europium leads to the formation of a monometallic tripodal complex, which has been characterised by X-ray crystallography. The luminescent and thermodynamic properties of the complexes along the lanthanide series will be discussed in view of potential applications for sensing purposes.



L1



L2

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Magnetic Properties of Metal Doped Zinc Oxide Nanoparticles Synthesized by Microwave-assisted Non-aqueous Method

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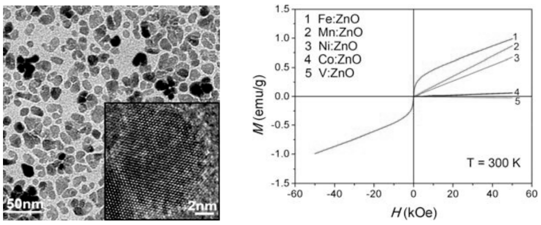
[b]Institute of Mathematics, Physics and Mechanics, Jadranska 19, 1000 Ljubljana, Slovenia

Dilute magnetic semiconductors (DMS) have attracted considerable attention due to their great potential applications in spintronics, which could consume less electricity and be more effective for computations than today's electronic devices [1]. With a wide bandgap of 3.4 eV and large exciton energy of 60 meV, zinc oxide (ZnO) is a promising host for DMS [2].

In this work, single-phase Co, Fe, Mn, V or Ni doped ZnO nanoparticles were successfully synthesized by microwave-assisted non-aqueous sol-gel processes [3]. Co, Mn, V or Ni doped ZnO nanoparticles show an antiferromagnetic behavior, whereas Fe doped ZnO shows ferromagnetism at 300K.



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155

Mesomorphic self-organization of $[Mn_{12}O_{12}(RCO_2)_{16}(H_2O)_4]$ Single Molecular Magnets

Emmanuel Terazzi[1], Bertrand Donnio[2], Jean-Louis Gallani[2], Guillaume Rogez[2], Benoît Heinrich[2], Cyril Bourgogne[2], Richard Welter[2], Daniel Guillon[2]

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[2] IPCMS, rue du Loess 23, F-67034 Strasbourg, France

The aim of molecular electronics is to use molecules as active entities in electronic devices with the basic idea that one (or several) molecule could achieve the same task as a classical electronic component. The principal advantage of such a "bottom-up" approach is mainly the miniaturization aspect. Many efforts of development were carried out during the last ten years, mainly in the field of information storage. The major breakthrough in this domain was the discovery of single molecular magnets (SMMs) in the early eighties. A few derivatives of the original $[Mn_{12}O_{12}(MeCO_2)_{16}(H_2O)_4]$ cluster were then synthesized but with poor results in term of organization so far, precluding any efficient addressing of the molecules. One way to organize a molecular entity is to control the intermolecular interactions. This approach is very often used in the field of liquid crystals. We have therefore designed several $[Mn_{12}O_{12}(R)_{16}(H_2O)_4]$ derivatives in which the peripheral groups (R) were systematically modified to give various molecular geometries and interfaces compatible with liquid crystals constraints [1] [2]. The compounds were fully characterized and found to exhibit interesting liquid crystalline properties. Furthermore, it was shown that the original magnetic behavior of the parent compound was preserved.

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Highly Luminescent Europium Complexes with Benzimidazole-Substituted Pyridine-2-Carboxylic Acids

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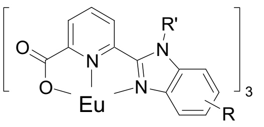
A facile synthesis of benzimidazole-substituted pyridine-2-carboxylic acids has been developed. These tridentate ligands efficiently sensitize europium luminescence in homoleptic neutral nine-coordinate complexes with overall quantum yields and lifetimes reaching 73% and 3.0 ms, respectively, in solid state at ambient conditions [1]. The simple modification of the ligands opens the way for incorporation of their complexes in electro-/luminescent materials.



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Efficient Near-Infrared Luminescence of Ytterbium Complexes with Benzoxazole-Substituted 8-Hydroxyquinolines

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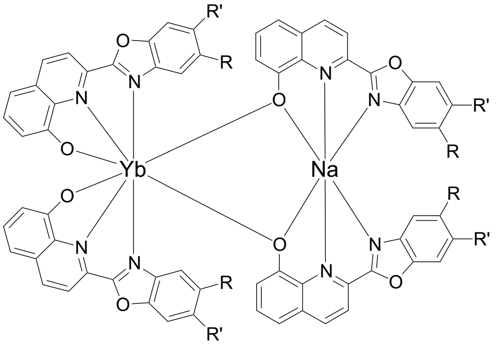
Hetero-binuclear Na^{I}-Yb^{III} complexes with benzoxazole substituted 8-hydroxyquinolines [1] display surprisingly efficient near-infrared emission of ytterbium at 925-1075 nm. The corresponding luminescence lifetime and quantum yield reach 22 μs and 3.7%, in the solid state, and 20 μs and 2.6% in 10^{-3} M CH_2Cl_2 solution [2].



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E$_c$-1 from wheat: exploring a unique metallothionein

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Metallothioneins (MT) are small proteins that act as proteic metal ion chelators. *Triticum aestivum* (wheat) **e**arly **c**ysteine labeled protein (E$_c$-1) was the first MT reported in higher plants.[1] This seed-specific protein presents a total of 17 Cys residues and has been shown to bind six divalent metal ions (M^{II}) in two separated metal-binding domains.[2] E$_c$-1 has unique and distinct structural properties, which were never observed before in any other MT. In the γ-domain of E$_c$-1,[3] apparently a metal-thiolate cluster with the stoichiometry $M^{II}_2Cys_6$ is formed, while the four M^{II} ions in the β_E-domain are organized in a $M^{II}_3Cys_9$ cluster and a mononuclear $M^{II}Cys_2His_2$ site.[4] Results from our latest biochemical and mass spectroscopic investigations of E$_c$-1 will be presented with an emphasis on metal exchange phenomena. In addition, we will show a comparison between the Zn^{II}-release properties of E$_c$-1 and other plant and vertebrate MTs. - Support from the Swiss National Science Foundation is gratefully acknowledged: SNF grant 200020-113728/1 and SNF Förderungsprofessur PP002-119106/1 to E.F.

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Metal binding ability and stability of a metallothionein from *Synechococcus vulcanus*

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Metallothioneins (MTs) constitute a family of small proteins (<10 kDa) with a high percentage of cysteine thiolate groups and a large metal ion content [1]. Their function is not finally resolved yet, but has been related to the regulation of physiological relevant metal ions (Zn^{II} and Cu^{I}) as well as to the protection against metal ion toxicity and oxidative stress.

The metallothionein of the thermophilic cyanobacterium *Synechococcus vulcanus* contains a total of 55 amino acids, among them 10 Cys and 2 His residues [2]. So far, no informations are available with respect to the metal ion binding capability and stability of the protein.

In the present work we show the ability of this MT to coordinate up to four divalent metal ions such as Cd^{2+}, Zn^{2+}, and Co^{2+} by UV-Vis and CD spectroscopy as well as mass spectrometry and the determination of the apparent pK_a values of the Cys residues in presence of the respective metal ions. We will put a special emphasis on the temperature-dependence of metal ion binding as this cyanobacterium finds optimal growth conditions in an environment of 55°C. A possible aggregation of the protein is investigated with dynamic light scattering.

Financial support by the Swiss National Science Foundation (SNF grant 20-113728/1 and SNF- Förderungsprofessur PP002-119106/1 to E.F.) is gratefully acknowledged.

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Carbohydrate-Based RAPTA Analogues

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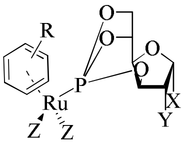
[b] Institute of Inorganic Chemistry, University of Vienna, Währinger Strasse 42, 1090 Vienna, Austria.

Recently, Ru^{II} organometallic compounds bearing the 1,3,5-triaza-7-phosphaadamantane (pta) ligand have attracted interest as anticancer agents, potentially enabling the treatment of tumors that are not curable by established platinum drugs. Replacing the pta ligand of RAPTA complexes by phosphorus containing carbohydrates affords new mono and dinuclear Ru^{II} complexes the in vitro anticancer activity of which has been investigated.



$X,Y = O_2C(CH_3)_2, O_2C_6H_{11}$; $X = SEt, NHAc$ $Y = OH$
$Z = Cl, Br, I, C_2O_4$
R = Me, *i*-Pr; CH_2CH_2OH; OCH_2CH_2OH; CH_2NH_3Cl; $CH_2CH_2NH_3Cl$

In vitro anticancer studies revealed that the 3,5,6-bicyclophosphite-1,2-O-cyclohexylidene-α-D-glucofuranoside complex was the most cytotoxic compound in human cancer cell lines (IC_{50} values around 30 μM depending on the cell line). The activity of the Ru complexes in non-tumorigenic cells was lower than in the tumor cell lines, which is an indication for a certain degree of selectivity towards malignant cells.

The authors are indebted to the EU for a Marie Curie Intra European Fellowship within the 7th European Community Framework Programme project 220890-SuRuCo (A.A.N.) and the Higher Education Commission of Pakistan (M.H.)

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Bifunctional N-Heterocyclic Carbenes: Multistage Switching in Benzo-(Bisimidazolylidene) Complexes?

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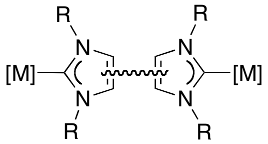
Molecular switches represent an attractive class of functional entities [1]. Multistage switching may be accessible by connecting two transition metal based active sites with a spacer that allows for a certain degree of electronic communication [2].
Earlier, we have shown that the bonding of N-heterocyclic carbenes (NHCs) to metal centers can reveal substantial metal-to-carbene π backbonding [3]. Accordingly, carbene-based spacers might be suitable for interconnecting two redox-active metal centers (see Figure) [4].



Here, we present our progress in using such bifunctional NHC ligands as spacers in binuclear complexes. Specifically, we will focus on the quality of different carbene spacers, which has been probed by measuring the spectroscopic and electrochemical characteristics of the bimetallic systems.

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[2] B. S. Brunschwig, C. Creutz, N. Sutin, *Chem. Soc. Rev.* **2002**, *31*, 168.
[3] L. Mercs, G. Labat, A. Neels, A. Ehlers, M. Albrecht, *Organometallics* **2006**, *25*, 5648.
[4] L. Mercs, A. Neels, M. Albrecht, *Dalton Trans.* **2008**, 5570.

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New luminescent europium complexes with long excitation wavelength

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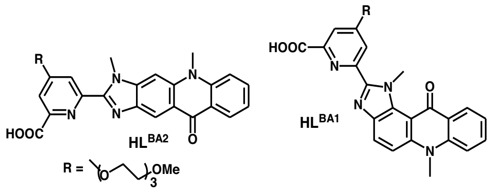
Several europium complexes, including very stable neutral homobimetallic [$Eu_2(L^{CX})_3$] (X=1-6) helicates [1], have been studied by our group with the aim of providing them as luminescent biological probes in aqueous media. One of the actual challenges consists in circumventing the intrinsic limitations of energetic UV-light excitation. Indeed, excitation below 340 nm suffers of several drawbacks for *in cellulo* applications including cell-damaging, need for costly quartz optics, and increased auto-fluorescence.

Acridone ring is known to sensitize Eu^{III} luminescence, *via* the commonly observed singlet-to-triplet conversion and the subsequent ligand-to-Eu^{III} energy transfer with excitation wavelength above 400 nm [2]. In the present work, we have kept intact the tridentate coordinating unit present in the former helicates with the concomitant fusion of both acridone and benzimidazole rings on the 6,7 or 7,8-positions of the latter heterocycle. After complexation with Eu^{III}, these ligands afford [$Eu (L^{BAX})_3$] (X=1 or 2) complexes. Additional organic and water-solubility is ensured by the presence of a polyoxyethylene chain on the 4-position of the pyridine heterocycle. We report here on the physico-chemical as well as photophysical properties of this new class of nonadentate Eu^{III} complexes.



[1] E. Deiters, B. Song, A.-S. Chauvin, C. D. B. Vandevyver, F. Gumy, J.-C. G. Bünzli, *Chem. Eur. J.*, **2009**, *15*, 885.
[2] A. Dadabhoy, S. Faulkner, P. G. Sammes, *J. Chem. Soc., Perkin Trans. 2,* **2002**, *2*, 348.

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Aminophosphine-Based Pincer Complexes of Palladium as Highly Efficient Catalysts for C,C-Cross-Coupling Reactions

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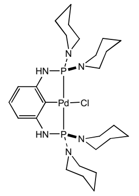
The aminophosphine-based palladium pincer complexes **1** and **2** are readily prepared from cheap starting materials in "one pot".[1] In general, these catalyst solutions can be used directly for catalysis without further purification.



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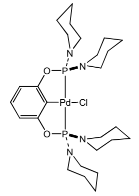
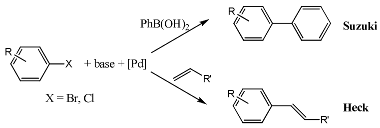


2

Complex **1** and **2** proved to be highly efficient catalysts for palladium catalyzed C,C-cross-coupling reactions such as the Suzuki and Heck reactions: Very low catalyst loadings and short reaction times are required for the quantitative coupling of several electronically deactivated and sterically hindered aryl bromides with phenylboronic acid or various olefins.[1-2]



[1] J.L. Bolliger, O. Blacque, C. M. Frech, *Angew. Chem. Int. Ed.* **2007**, *46*, 6514.
[2] J.L. Bolliger, O. Blacque, C. M. Frech, *Chem. Eur. J.* **2008**, *14*, 7969.
[3] J.L. Bolliger, C. M. Frech, *Adv. Synth. Catal.* **2009**, *351*, 891.

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Overcoming limitations of lanthanide luminescent bioprobes

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[1] École Polytechnique Fédérale de Lausanne (EPFL), Laboratory of Lanthanide Supramolecular Chemistry, BCH 1402, 1015 Lausanne, Switzerland.
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Recently, many unique advantages of using bimetallic triple helicates as lanthanide luminescent bioprobes (LLB) have been demonstrated.[1] In this work we explore enlarging the capability of these compounds by using multi-photon excitation and by formation of surface-functionalized nanoparticles. In particular, [$Ln_2(L^{C2})_3$] (Ln = Eu^{III}, Tb^{III}) [2] and [$Eu_2(L^{C5})_3$] [3] were found to exhibit three- and two- photon sensitized luminescence, respectively, when excited at 800 nm by a femtosecond laser. Moreover, with the idea of increasing the sensitivity of LLBs, [$Eu_2(L^{C2})_3$] was encapsulated into silica nanoparticles (~60 nm) the surface of which was functionalized with –SH or –NH_2 groups. The photophysical properties remain adequate for [$Eu_2(L^{C2})_3$]@SiO_2/–SH with almost the same overall quantum yield (20%) and lifetime (3.1 ms) compared with surface-unmodified nanoparticles (25%, 3.4 ms), while for [$Eu_2(L^{C2})_3$]@SiO_2/–NH_2 a significant decrease in Q^{L}_{Eu} was observed. Thus, [$Eu_2(L^{C2})_3$]@SiO_2/–SH can be considered to be a promising precursor for further bioconjugation with proteins and *in cellulo* tests.

[1] J.-C. G. Bünzli, *Chem. Lett.* 2009, *38*, 104.
[2] J.-C. G. Bünzli, A.-S. Chauvin, C. D. B. Vandevyver, B. Song, S. Comby, *An. N. Y. Acad. Sci.* 2008, *1130*, 97.
[3] E. Deiters, B. Song, A.-S. Chauvin, C. Vandevyver, J.-C. G. Bünzli, *Chem. Eur. J.* 2009, *15*, 885.

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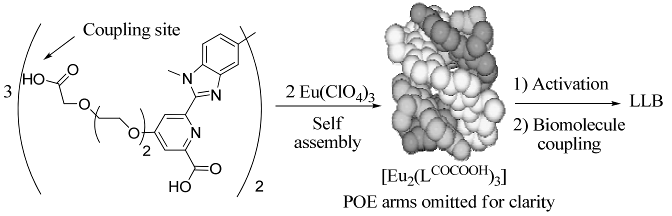
Bioconjugated Lanthanide Helicates: Synthesis and Applications.

Vanesa Fernández-Moreira, Bo Song, Anne-Sophie Chauvin, Caroline D. B. Vandevyver, Jean-Claude G. Bünzli.

École Polytechnique Fédérale de Lausanne, Laboratory of Lanthanide Supramolecular Chemistry, BCH 1402, CH-1015 Lausanne (Switzerland).

The ever growing interest for lanthanide complexes as luminescent bioprobes (LLB) is due to their extraordinary photophysical properties such as line-shape emission, insensitivity to photobleaching, and long excited level lifetimes. The latter allow to overcome intrinsic problems to commercially available organic fluorophores (e.g. autofluorescence or photobleaching). Moreover, the development of LLBs opens the door to using new available technologies such as time-resolved detection and multi-photon excitation, which can be helpful tools in medical analyses and diagnostic [1].

Herein we present a highly thermodynamically and kinetically stable lanthanide helicate [2] modified to covalent link biomolecules such as proteins or peptides. Applications of the luminescent lanthanide bioprobes will be presented and their potentiality discussed.



[1] J.-C. G. Bünzli, *Chem. Lett.,* **2009**, *38*, 104.
[2] J.-C. G. Bünzli, A.-S. Chauvin, C. D. B. Vandevyver, S. Comby, *Ann. N.Y. Acad. Sci.*, **2008**, *1130*, 97.

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Simultaneous Synthesis of Nanoparticles and Film Deposition by Microwave Assisted Nonaqueous Sol-Gel Route

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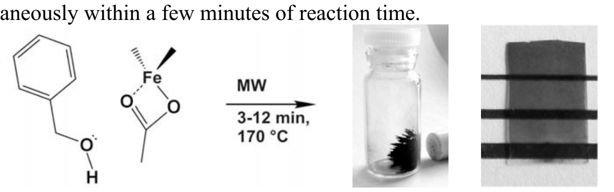
The microwave (MW) assisted nonaqueous sol-gel route offers a simple approach to a wide range of highly crystalline metal oxide nanoparticles with tunable size and composition at moderate temperatures [1,2]. This route can also be exploited for tailored film deposition, controlled by simple experimental parameters. The advantage of this process is that the synthesis of well defined nanoparticles and the coating of glass substrates occur simultaneously within a few minutes of reaction time.



Applied to multiferroics, the process offers a promising low cost route for various ferrite-layers, namely MFe$_2$O$_4$ M=Fe,Co,Mn,Ni,Ti. The combination of CoFe$_2$O$_4$ with BaTiO$_3$ deserved special attention as this system was reported to lead successfully to multiferrocity [3].

This work gives an overview of the synthesis routes involved, the *in situ* film deposition as well as the characterization of selected compounds.

[1] I. Bilecka, P. Elser and M. Niederberger, *ASC Nano*, **2009**, *3*, 467-477.
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Understanding the Reactivity of Cyclopentadienyl Coordinated Ruthenium β–Diketiminate Complexes

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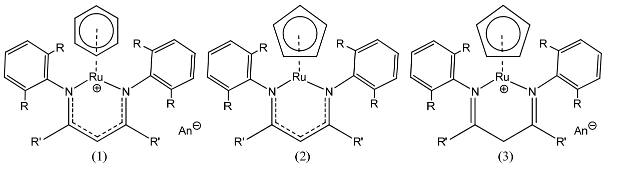
(a) Institut des Sciences et Ingénierie Chimiques, Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland.
(b) Laboratorium für Anorganische Chemie, ETHZ HCI Hönggerberg CH-8093 Zürich.
(c) School of Chemistry and Chemical Biology, University College of Dublin, Belfield, 4 Dublin, Ireland.

β-diketiminates are rapidly becoming the ideal ligand for stabilizing coordinatively unsaturated transition metal complexes. Previously some of us have reported on the synthesis, characterization and catalytic capabilities of a series of η^6-arene Ru-*β*–diketiminate complexes of type **1**.[1] We continue to explore the reactivity of other Ru-*β*–diketiminate species, **2**, now supported by a η^5-cyclopentadienyl group. A selection of different reactions involving small unsaturated molecules including O$_2$, CO and other systems containing a C=C or P≡C multiple bond are reported. Moreover, interesting results have been obtained through the addition of a solid acid to **2**, affording the highly reactive 16 electron ruthenium species (**3**). Characterization and reactivity studies are presented in conjugation with DFT calculations which examine the differences in electronic structure between **2** and **3**.



[1] Phillips, A. D., Dyson, P. J. *et. al. Organometallics*, **2007**, *26*, 1120.

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Synthesis and characterisation of the first isoxazolylidene: assessment of its donor properties and catalytic activity

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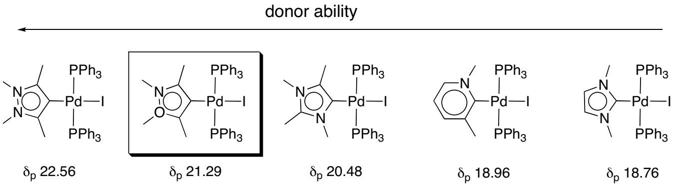
Ch. du Musee 9, CH-1700 Fribourg, SWITZERLAND

The oxidative addition of relatively inert organic bonds is the rate-determining step for many catalytic transformations. Examples include C-H activation for alkane oxidation or H$_2$ activation for hydrogenation reactions. These reactions are generally promoted by an increase of the electron density at the metal centre, which can be achieved by providing the metal with strong electron donating ligands.

Encouraged by the pioneering work of Raubenheimer's and Huynh's research groups on developing highly basic remote *N*-heterocyclic carbenes,[1] we prepared the first 4-isoxazolylidene. In this poster presentation, the synhetic route to its palladium(II) complex will be presented together with an assessment of its basicity using ^{31}P NMR shifts and calculations as probes.



n addition, we will compare the catalytic activity of these complexes in cross-coupling reactions.

1] (a) S. K. Schneider, P. Roembke, G. R. Julius, C. Loschen, H. G. Raubenheimer, G. Frenking, W. A. Herrmann, *Dalton Trans.*, 2006, 1226. b) Y. Han, H. V. Huynh, *Chem Commun.*, 2007, 1089.

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Aqueous syntheses of [(Cp-R)M(CO)$_3$] type complexes (Cp = cyclopentadienyl, M = Mn, ^{99m}Tc, Re) with bioactive functionalities

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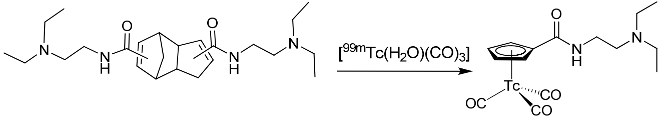
Cyclopentadienyl (Cp$^-$) is a basic ligand in organometallic chemistry. It is highly relevant for radiopharmaceutical research since it has a low molecular weight, it blocks three coordination sites, includes the possibility of conjugating targeting vectors and forms robust and "innocent" d^6 organometallic [(Cp-R)M(CO)$_3$] (M = Re, Tc) complexes. Additionally, these kind of piano-stool compounds have been shown to mimic arene rings in some biological systems [1]. For radiopharmaceutical applications on a routine base, it is desirable to prepare e.g. [(Cp-R)^{99m}Tc(CO)$_3$] directly in water. We published a fully aqueous synthesis of [(Cp-R)^{99m}Tc(CO)$_3$] at <100 °C. Using a carboxylate derived Diels-Alder product of cyclopentadiene, we proposed the retro Diels–Alder reaction with the [^{99m}Tc(CO)$_3$]$^+$ core to be metal mediated, resulting in a {(η^5-Cp)Tc} core, where the carboxylate serves as a preliminary anchoring group [2].



Here we report now about an important extension to the previous work. Replacing a phenyl ring by [(Cp-R)M(CO)$_3$] we introduce several organometallic model compounds with Mn or Re, based on well known pharmaceuticals with amide functionality and also exact structural analogs of these aromatic organic drugs. We show that amides can also act as anchoring group and the corresponding ^{99m}Tc complexes can be synthesized along a retro Diels–Alder reaction.

[1] R. P. Hanzlik, P. Soine et. al, *J. Med. Chem.*, **1979**, 22, 424.
[2] Y. Liu, B. Spingler, et. al, *J. Am. Chem. Soc.* **2008**, 130, 1554.

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A cytotoxic ruthenium tris(bipyridyl) complex that accumulates at plasma membranes

Olivier Zava, Shaik M. Zakeeruddin, Christophe Danelon, Horst Vogel, Michael Grätzel and Paul J. Dyson

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Ruthenium tris(bipyridyl) complexes in which the bipyridyl ligand is derivatized with groups exhibiting different lipophilicities have been evaluated *in vitro*. A complex in which the ligand is derivatized with a diethylamine group, Ru(DEA-bpy)$_3$, was shown to be both the most lipophilic and cytotoxic compound, whereas the less lipophilic compounds are not cytotoxic.

Due to the intrinsic fluorescence of the complexes, confocal microscopy was used to gain insights into the uptake and localisation of the luminescent complexes in cells, with an emphasis on the early events in their internalisation. The most lipophilic complex, Ru(DEA-bpy)$_3$, adhered to the plasma membrane whereas the other complexes penetrated the membrane and accumulated in small organelles in the cytoplasm. Moreover, at high concentration of Ru(DEA-bpy)$_3$, the complex accumulated mainly at the plasma membrane and was rather poorly internalised, whereas at lower concentrations, the complex was efficiently internalised, following a rapid, energy-independent membrane accumulation.

These results suggest two alternative routes of cell internalisation of this class of metal complexes. This study participates in a relatively recent effort of the scientific community to question cytotoxicity of metal complexes by studying their uptake [1]; notably none of the compounds appear to accumulate in the cell nucleus which questions the relevance of DNA as a target for this class of compound [2, 3].

[1] C. A. Puckett and J. K. Barton, *Biochemistry* **2008**,
[2] V. Brabec and O. Nováková, *Drug Resistance Updates* **2006**, *3*, 111-122
[3] P. J. Dyson and G. Sava, *Dalton Trans* **2006**, *16*, 1929-33

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New Ligands for Photochromic Spin Crossover Complexes

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Our group is active in the synthesis of photochromic ligands.[1] Organic dithienylethene derivatives have been extensively studied because of their potential applications in the field of photochromic and photonic devices.[2] Various iron(II) tris(diimine), bis(diimine) and bis(terimine) systems on the other hand were reported to undergo a temperature dependent spin crossover process.[3] In this context it is highly interesting to use photochromic switches incorporated in diimine or terimine ligands. Assuming that the photoactive opening and closing process of the ligand system changes the ligand field properties sufficiently, we should obtain a system that undergoes a spin crossover upon irradiation with light at room temperature. This concept has already been studied by a few other groups and was called ligand-driven light-induced spin change LD-LISC.[4,5]

[1] Kuhni, J.; Adamo, V.; Belser, P. *Chimia*, **2006,** *60,* 207-211.
[2] Irie, M. *Chem. Rev*., **2000**, *100,* 1685-1716.
[3] Top Curr Chem., **2004**, *233*, 59-90
[4] Kolb, J. S.; Thomson, M. D.; Novosel, M.; Senechal-David, K.; Riviere, E.; Boillot, M.-L.; Roskos, H. G. *Comptes Rendus Chimie*, **2007**, *10,* 125-136.
[5] Hasegawa, Yuta; Kume, Shoko; Nishihara, Hiroshi. *Dalton Transactions*, **2009**, *2*, 208-284.

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A simple preparation of an efficient and recyclable heterogeneous gold catalyst for the aerobic oxidation of amines

Linda Aschwanden, B. Panella, Tamas Mallat, Frank Krumeich, Alfons Baiker

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Most of heterogeneous gold catalysts for aerobic oxidations are prepared in a similar way: a gold salt, most generally $HAuCl_4$, is applied onto the surface of a support and then this precursor is transferred into the active gold nanoparticles by calcination or reduction [1]. The last two steps are normally difficult to carry out in a synthetic chemical laboratory, not equipped for the preparation of heterogeneous catalysts. Therefore, our aim was to find a simple and efficient way to synthesize active gold catalysts for aerobic oxidations.

The method was developed by studying the oxidation of amines to imines, which is an important transformation since imines are crucial intermediates in the synthesis of biologically active nitrogen compounds [2]. A very simple synthetic route was found, in which case there is no need for any *ex situ* preparation steps of the catalyst, such as impregnation, calcination or reduction, since the active gold nanoparticles are formed *in situ* [3]. In addition, the activity of the catalyst is comparable to or better than those of formerly published or commercially available catalysts. The method can be applied to the oxidation of various amines to imines. Further developments resulted in a magnetically separable and recyclable system by using superparamagnetic ceria/iron oxide nanoparticles as the support.

[1] A. S. K. Hashmi, G. J. Hutchings, *Angew. Chem. Int. Ed. Engl.* **2006**, *45*, 7896.
[2] J. S. M. Samec et al., *Chem. Eur. J*,. **2005**, *11*, 2327.
[3] L. Aschwanden T. Mallat, F. Krumeich, A. Baiker, , *J. Mol. Catal. A: Chem.*, **2009**, accepted

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Chiral Macrocyclic PNNP ligands for Asymmetric Catalysis

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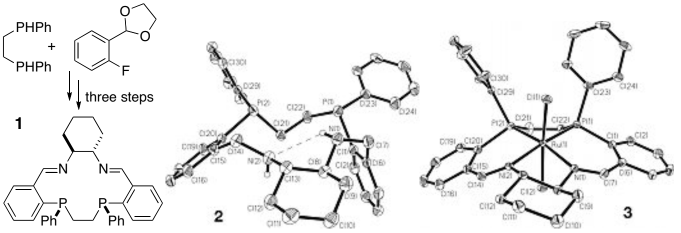
Chiral macrocyclic ligands containing P donors are highly interesting for asymmetric catalysis as they are expected to form stable, conformationally rigid complexes. However, owing to the challenges posed by they synthesis, they are still rare.[1] We developed a straightforward synthesis to the first chiral macrocyclic PNNP ligand (**1**), which is easily reduced to the diamino analogue **2**, and prepared their ruthenium(II) dichloro complexes:[2]



The macrocycle cavity can host a 4d metal ion such as ruthenium(II), as indicated by the average P···N distances of 4.26 Å in $[RuCl_2(\mathbf{1})]$ (**3**), but with exceptionally short Ru–P distances (2.204(1) and 2.213(1) Å). The diimino complex **3** catalyzes the transfer hydrogenation of acetophenone to 1-phenylethanol with modest enantioselectivity (30% ee). The low enantioselection is not surprising in view of the pseudo meso relationship between the P atoms. Therefore, our efforts are presently directed to the synthesis of C_2-symmetric PNNP macrocycles. Further synthetic developments and catalytic applications will be reported.

[1] Caminade, A. M.; Majoral, J. P. *Chem. Rev.* **1994**, *94*, 1183.
[2] Ranocchiari, M.; Mezzetti, A. *Organometallics* **2009**, *28*, 1286.

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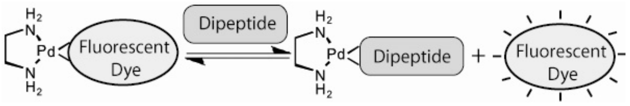
A Fluorescent Chemosensor for the Identification of Dipeptides in Aqueous Solution at Neutral pH

Jie Gao[1,2], Sébastien Rochat[1], Xuhong Qian[2], Kay Severin[1*]

1 Institute of Chemical Sciences and Engineering, Swiss Federal Institute of Technology Lausanne (EPFL), CH-1015 Lausanne, Switzerland
2 Shanghai Key Laboratory of Chemical Biology, School of Pharmacy, East China University of Science and Technology, 200237 Shanghai, China

Indicator displacement assays (IDAs) based on $[Cp^*RhCl_2]_2$ as receptor have been used to detect biologically interesting analytes [1][2]. We demonstrate herein that the combination of $Pd(en)Cl_2$ with several fluorescent dyes comprise fluorescent indicator displacement assays (FIDAs), which allow the identification and quantification of dipeptides in aqueous solution at neutral pH.



The Pd receptor is bound to the fluorescent dyes through noncovalent interactions. The association constants between the palladium complex and different dyes were determined by fluorescence titration experiments. The metal-dye complexes are able to undergo ligand-exchange reactions with dipeptides, which could be detected by the changes of the fluorescence signal. When performed in an assay format, the displacement assays allowed to distinguish low micromolar concentrations of dipeptides with high fidelity.

[1] Buryak A. and Severin K., *Angew. Chem. Int. Ed.* **2004**, *43*, 4771.
[2] Buryak A. and Severin K., *J. Am. Chem. Soc.* **2005**, *127*, 3700.

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Photocatalytic Hydrogen Production with a Rhenium/Cobalt System: Understanding the longterm Performance

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University of Zurich, Winterthurerstr. 190, CH-8057 Zurich

Previously, a detailed mechanistic investigation from our lab showed that $[ReBr(CO)_3bipy]$ (**1**) and $[Co(dmgH)_2]$ (**2**) in DMF serve as an efficient photocatalytic system for hydrogen production.[1] A detailed mechanistic investigation will be presented which allowed us to identify the rate limiting steps and to increase the TON of the system substantially (Figure 1).

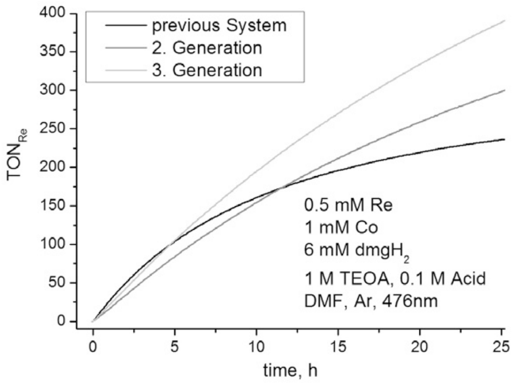

Figure 1: Improvement in hydrogen production when going from the 1st to the 3th generation of catalysts.

[1] Probst, B.; Kolano, C.; Hamm, P.; Alberto, R. *Inorg. Chem.* **2009**, *48*, 1836-1843.

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Macrocyclic cobalt complexes for homogenous photocatalytic H_2 production

Miguel Guttentag, Benjamin Probst, Alexander Rodenberg, Peter Hamm, Roger Alberto

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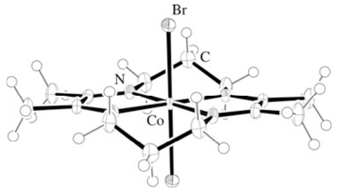
We recently reported a mechanistic investigation of a rhenium-cobalt based system in DMF for photocatalytic H_2 generation. [1] Our ongoing research aims at increasing the stability and productivity of the catalytic cobalt cycle to improve *her*-catalysis. So far, the prototype $Co(dmgH)_2$ was substituted by the cobalt tetraaza macrocycle CoTIM (see structure) and further Cobalt complexes.



All complexes have been characterized by x-ray crystallography. Hydrogen evolution experiments were performed and showed catalytic activity for all the investigated complexes. Reaction conditions as cobalt concentrations and pH were varied. Preliminary kinetic results indicate a heterolytic hydrogen release, which stands in contrast to the results for the $Co(dmgH)_2$ system. [1] Improvement of the stability of the complexes and their higher activity during catalysis will be presented.

[1] Probst, B.; Kolano, C.; Hamm, P.; Alberto, R., *Inorg. Chem* **2009,** 48, (5), 1836.

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Mechanistic Studies on the Atom Transfer Radical Addition (ATRA) of chlorinated compounds to olefins catalyzed by Ru-Cp* complexes

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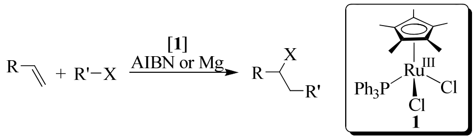
The atom transfer radical addition (ATRA) of halogenated compounds to olefins represents a versatile C-C coupling reaction with many applications in organic synthesis. The highest activities for the catalytic version of this process are typically found for copper and ruthenium complexes.
One of the best catalysts described so far is the halfsandwich complex [$RuCl_2Cp^*(PPh_3)$] (**1**) which has showed excellent activities for a wide variety of substrates when used with AIBN or Mg as co-catalyst.[1]



However, despite the substantial efforts that have been invested to optimize the performance of Ru-based ATRA catalysts, there are hardly any mechanistic studies on this process apart from some early kinetic investigations with the first generation catalyst [$RuCl_2(PPh_3)_3$].[2] In this work, we present an in-depth mechanistic study on the ATRA reactions of different chlorinated substrates with styrene catalyzed by complex **1** with Mg as a co-catalyst, disclosing the relative influence of the different steps of the cycle on the reaction rate, as well as the resting state of the catalyst.

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[1] (a) L. Quebatte, K. Thommes, K. Severin, *J. Am. Chem. Soc.* **2006**, *128*, 7440. (b) K. Thommes, B. Içli, R. Scopelliti, K. Severin, *Chem. Eur. J.* **2007**, *13*, 6899.
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Changing the Chemical Behavior of Ru Half-Sandwich Complexes with a Sterically Demanding Cyclopentadienyl Ligand

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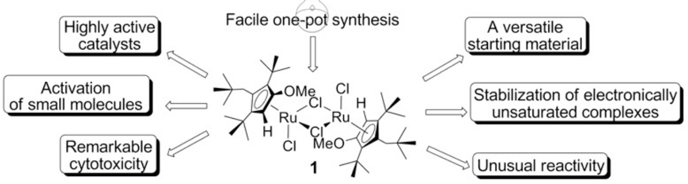
Cp or Cp* based Ru half-sandwich complexes are extensively used owing to their easily available precursors. But, structurally modified cyclopentadienyl ligands being relatively uncommon, the significance of the π-ligand remains largely unexplored. Towards this end, we have reported the one-pot synthesis of complex **1**, bearing a highly substituted cyclopentadienyl ligand, through a Ru-mediated [2+2+1] cyclotrimerization of *tert*-butylacetylene[4].



It is a highly suitable starting material giving access to a variety of complexes through ligand substitution[3], while at times exhibits substantially different reactivity. Some complexes are more active catalysts in ATRC[2] or cycloaddition reactions or as cytotoxic as cisplatin[1]. Electronically unsaturated complexes, some being proposed reaction intermediates, have been stabilized[3, 2] and activation of interesting small molecules was achieved.

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[2] B. Dutta, R. Scopelliti, K. Severin, *Organometallics*, **2008**, *27*, 423.
[3] B. Dutta, E. Solari, S. Gauthier, R. Scopelliti, K. Severin, *Organometallics*, **2007**, *26*, 4791.
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Coordination Chemistry of Bidentate Triazolopyridines and other Azole Ligands

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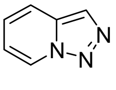
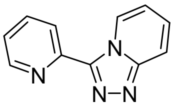
Although the first silver complexes of [1,2,3]triazolo[1,5-*a*]pyridine (**I**) were mentioned as early as 1957,[1] the coordination chemistry of triazolopyridines has not attracted much attention up to date. This situation is particularly surprising given that N-heterocyclic aromatics in general are well known to form spin-crossover (SCO) complexes with iron(II) salts quite frequently.[2]

The coordination behaviour of the bidentate azole ligand 3-(2-pyridyl)-[1,2,4]triazolo[4,3-*a*]pyridine (**II**) has been studied and complexes with iron(II), cobalt(II), nickel(II) and copper(II) have been structurally characterized. The SCO phenomenon is observed in iron(II) complexes of **II** and related bidentate azole-based ligands.



I



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180

Synthesis and Characterization of Dinuclear Complexes with the Bridging Ligand TTF-ppb

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To study the interactions between two paramagnetic metal ions mediated through redox-active tetrathiafulvalene(TTF) derivatives, the bridging ligand, TTF-fused dipyrido [2,3-*a*:3′,2′-*c*]phenazine (ppb), was chosen. Starting from the mononuclear [Co(II)(TTF-ppb)(hfac)$_2$] (hfac=hexafluoroacetylacetonate) compound, dinuclear complexes [Co(II)M(II)(TTF-ppb)(hfac)$_4$] (M=Ni(II) and Cu(II)) have been synthesized and structurally characterized. Their electrochemical properties and magnetic behaviors are investigated.

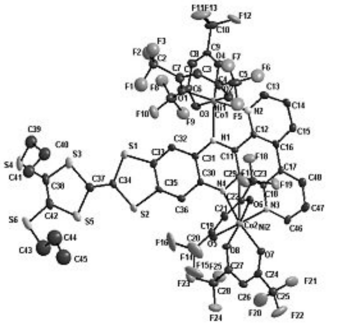

Figure 1. Crystal structure of the complex [Co(II)Ni(II)(TTF-ppb)(hfac)$_4$]. Hydrogen atoms and solvent molecules are omitted.

References:

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Ligand-Mediated Decarbonylation (LMD) as a General Synthetic Route to Rhenium (I) and Rhenium (II) Dicarbonyl Complexes

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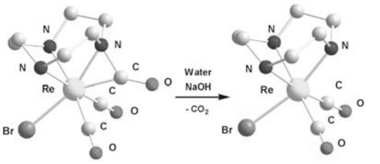
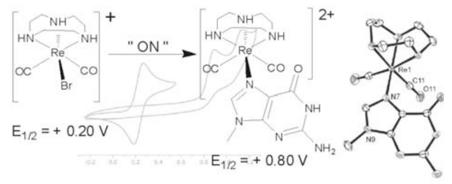
Rhenium (II) chemistry (d^5 configuration) is rare. This is surprising since the related paramagnetism together with the open shell electronic configuration makes such complexes highly interesting for applications in medicine, magnetochemistry or catalysis.[1] We have developed a general chemical procedure which allows, starting from common *fac*-$[Re(CO)_3L_3]$ complexes, to efficiently decarbonylate the metal core yielding stable *cis*-$[Re(CO)_2L_4]$ species (**A**).[2] Compared to the parent molecule, these species show a drop in the $Re^I \rightarrow Re^{II}$ oxidation potential of ca. 1.2V making Re(II) complexes readily available. These in turn behave as bio-inducible redox switches (**B**).



(**A**)



(**B**)

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Structural characterization of a high active superoxide-dismutase mimic

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The synthesis of low molecular weight copper complexes with superoxide dismutase activity, named SOD-mimics, represents an approach to avoid the drawback of SOD in pharmaceutical applications. Here, we characterized the metal coordination sphere in one high active SOD-mimic based on 6-(2-hydroxy-benzaldehyde) hydrazono-as-triazine-3,5-dione, in order to understand which conformation promotes a high SOD-like activity.

X-ray diffraction reveals a dinuclear structure in the solid state. However, in solution, the dinuclear complex is broken, forming a mononuclear copper center as obtained from UV/Vis spectroscopy and electron paramagnetic resonance (CW-EPR) experiments. In order to obtain more detailed information, a number of pulsed EPR experiments were set up (ESEEM, ENDOR, ELDOR-detected NMR), and were completed by DFT calculations using five different models of Cu^{II}SODm. All observed EPR and DFT data indicate a five coordination sphere around copper ion with axial and equatorial ligation of solvent molecules. This mono-nuclear conformation of the complex provides an easy accessibility to the O_2^- anion and thus contributes to its high catalytic activity.

Figure 1. Schematic representation of Cu^{II}SODm in solution.

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Synthesis of 6-substituted 2,2'-bipyridines and their application in iTCMs for LECs

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Light-emitting electrochemical cells (LECs) are alternatives for LEDs or OLEDs. They typically consist of a film of an ionic transition metal complex (iTCM) between two electrodes. One advantage of LECs is that they do not need electrodes with a high work function which allows the use of Al instead of Ca or Mg and the devices do not have to be sealed.

In our group, complexes of Ir have been studied intensively. For example, the presence 6-phenyl-2,2'-bipyridine (pbpy) in $[Ir(ppy)_2pbpy][PF_6]$ increases the lifetime of the LEC device, compared to $[Ir(ppy)_2bpy][PF_6]$ due to the -stacking of the phenyl with a 2-phenylpyridine (Hppy).

The aim of this work is to use bipyridines with heteroaromatic substituents and retain the stability of the complex due to the -stacking but hopefully also achieve a shift in the emission.

For this purpose the following series of 6-substituted 2,2'-bipyridine ligands has been synthesized and characterized:

Complexes with iridium will be described and tested for their suitability for LECs.

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Air- and Moisture Stable Ferrocene Based Secondary Phosphines as Versatile Precursors for New Ligands

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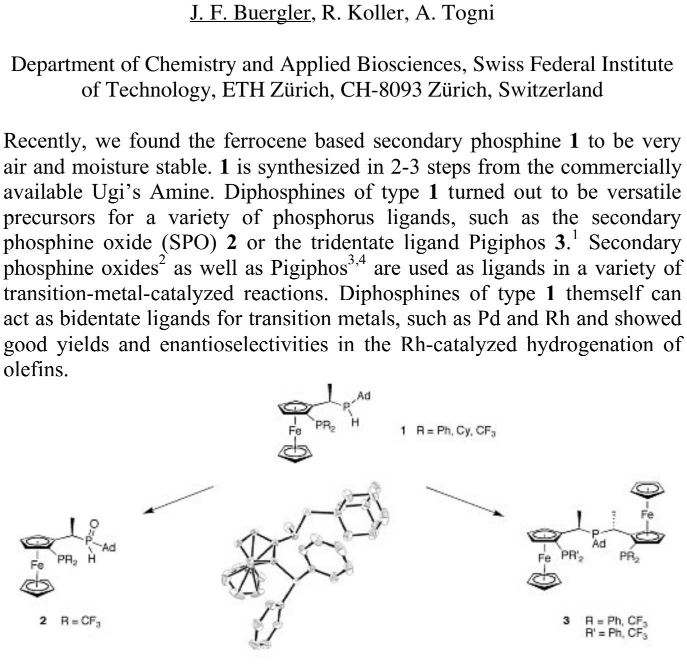
Recently, we found the ferrocene based secondary phosphine **1** to be very air and moisture stable. **1** is synthesized in 2-3 steps from the commercially available Ugi's Amine. Diphosphines of type **1** turned out to be versatile precursors for a variety of phosphorus ligands, such as the secondary phosphine oxide (SPO) **2** or the tridentate ligand Pigiphos **3**.[1] Secondary phosphine oxides[2] as well as Pigiphos[3,4] are used as ligands in a variety of transition-metal-catalyzed reactions. Diphosphines of type **1** themself can act as bidentate ligands for transition metals, such as Pd and Rh and showed good yields and enantioselectivities in the Rh-catalyzed hydrogenation of olefins.



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Determinant corrin-sidechains for switching a B_{12} riboswitch

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The function of riboswitches as RNA sensors for the control of gene expression is based on their direct interaction to cellular metabolites.[1] The very high specificity of this interaction and the occurrence of riboswitches in bacteria make this RNA class an ideal target for antimicrobial drugs.
The *btuB* riboswitch of *E. coli* regulates the expression of the outer membrane B_{12} transporter BtuB by binding to intracellular cofactor B_{12}. In contrast to the findings of initial studies,[2] the corrin ring of B_{12} with its many side-chains was demonstrated to be the crucial moiety to induce RNA rearrangement *in vitro*.[3] On the other hand, the presence of both large apical ligands increases the affinity significantly.
Acid-derivatives of vitamin B_{12} were therefore applied in spontaneous self-cleavage experiments of the RNA in order to identify the essential side-chains for a correct switch of the *btuB* riboswitch. We could show that the modification of a single amide-sidechain to a negatively charged acid moiety can have a large impact on the structural rearrangement of the RNA. While the modification of sidechain *e* prevents from a correct, concerted and complete restructuration, the modification at sidechain *c* induces structural changes of the riboswitch unrelated to the "wild-type" rearrangement. The correct hydrogen bonding properties of the corrin ring system are thus compulsory not only for a strong interaction but also for a correct rearrangement of the *btuB* riboswitch.

[1] W. C. Winkler, R. R. Breaker, *Annu. Rev. Microbiol.* **2005**, *59*, 487.
[2] A. Nahvi, N. Sudarsan, M. S. Ebert, X. Zou, K. L. Brown, R. R. Breaker, *Chem. Biol.* **2002**, *9*, 1043.
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Support by the Swiss National Science Foundation and by the University of Zürich is gratefully acknowledged.

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Dramatic influence of phosphoester versus phosphonate coordinating groups in the sensitization of lanthanide ions

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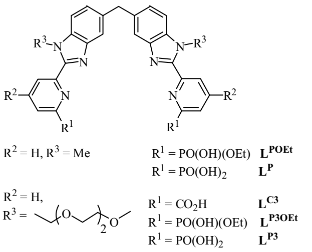
E-mail: anne-sophie.chauvin@epfl.ch



We aim at comparing the influence of phosphoester versus phosphonate coordinating units on lanthanide coordination ability and on the photophysical properties of the corresponding complexes. The series of ligands depicted in the figure differ from the previously reported ones [1,2] in their terminal coordinating units. This allow us to further compare carboxylate versus phosphonate or phosphoester coordination.

The synthesis of the different ligands and their self-assembly with lanthanide ions into binuclear helicates are described ($\log\beta_{23} \approx 21$-$24$ for the Eu^{III} complexes). Photophysical properties of the complexes are modulated by the nature of the coordinating group and quantum yield up to 25% in water can be obtained, while the lifetime of the $Eu(^5D_0)$ level reaches 4.5 ms.

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Luminescence of lanthanide tris-(6-phosphoryl picolinicates) versus trisdipicolinate.

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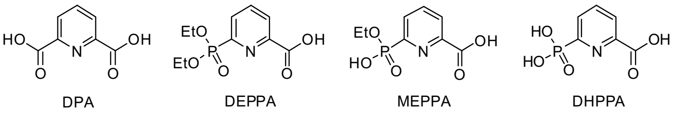
Derivatives of dipicolinic acid have shown great potential as efficient and stable lanthanide sensitizers. We propose here to replace one of the coordinating groups of dipicolinic acid by phosphoryl groups and to compare their photophysical properties to the well known lanthanide trisdipicolinate standard.
According to our results, in the ligand series diethoxy-, monoethoxy and dihydroxy-6-phosphoryl picolinic acid, diethoxyphosphoryl seems to be a better sensitizer than other phosphoryl groups. It shows as good solubility and complex stability as efficient quantum yield and rather high lifetime in slightly acidic aqueous solution. Therefore, complementary photophysical properties compared to tris(dipicolinate) complexes have been enlightened.



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RECENT DEVELOPMENTS IN PALLADIUM-CATALYSED ENANTIOSELECTIVE ALLYLIC PHOSPHINATION

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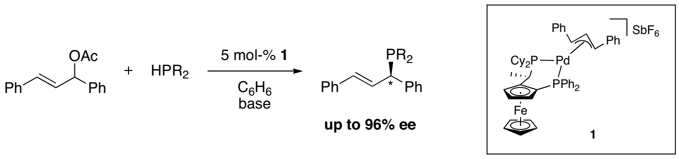
Palladium-catalysed allylic substitution reactions are known to occur with a variety of carbon, nitrogen and oxygen nucleophiles. Our group has recently reported an unprecedented allylation of secondary phosphines [1]. The model substrate 3-acetoxy-1,3-diphenylprop-1-ene reacts with diphenylphosphine to the corresponding allylic tertiary phosphine in the presence of triethyl amine and 5 mol-% of a Pd catalyst (**1**) containing the chiral ferrocenyl ligand *Josiphos*. We now found that the reaction can be drastically accelerated by an additional catalytic amount of stronger bases such as DBU or K_3PO_4. The allylic phosphine product is thereby isolated in high yield and enantioselectivity.



In order to investigate the role of DBU in the catalytic cycle, a DBU containing Pd-allyl complex was prepared and characterised by NMR and X-ray crystallography.

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New chiral salen ligands for hierarchical multicomponent assembly and asymmetric catalysis

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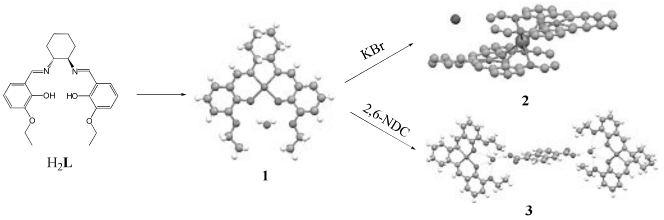
A long-term aim of supramolecular chemistry is the self-assembly of multifunctional systems with predefined properties.[1] In order to assemble such systems, it is necessary to deploy polyvalent building blocks with a variety of molecular recognition motifs. Here we describe two types of hierarchical structures resulting from two sequential metal-ligand bindings or from sequential metal-ligand and hydrogen bonding interactions, and the studies on enantioselective catalysis.

The ethoxy-pendant salen ligand with a chiral motif (H_2**L**) was used to synthesize simple Cu^{II} complex (**1**) with an additional water incorporated in the O, O', O'', O''' –cavity, which can either be replaced by an alkali metal (K^+), forming a sandwich-type heterotrinuclear complex (**2**), or be hydrogen-bonded to a bridging donor ligand naphthalene-2,6-dicarboxylic acid to result in a multicomponent assemble (**3**).[2] The Cu^{II} complex of both salen and reduced salen have been investigated for enantioselective Henry reaction.



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The Thermodynamics of Selenodisulfides

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The interplay between sulfur and selenium plays a vital role in selenoenzymes [1]. Nevertheless, the different oxidation states, especially the radical states, of alkyl selenodisulfides (RSe-SR) are poorly studied.

Here, we present the kinetics and thermodynamics of the reduction of several diselenides by their respective thiolates:

$$RSe\text{-}SeR + RS^- \rightleftharpoons RSe\text{-}SR + RSe^-$$

$$RSe\text{-}SR + RS^- \rightleftharpoons RS\text{-}SR + RSe^-$$

Selenium is a better nucleophile and a slightly better leaving group compared to sulfur.

By means of pulse radiolysis the radical cationic and anionic states of the oxidized dithiotreitol (DTT_{ox}), diselenotreitol ($DSeT_{ox}$) and selenothiotreitol ($SeTT_{ox}$) were generated. The radical anions can be protonated, and there is an equilibrium between the open and closed form. The radical $SeTT_{ox}^{\bullet-}$ is most basic (pK_a = 7.4) and at neutral pH mainly in the open-ring, protonated, form, whereas $DTT_{ox}^{\bullet-}$ and $DSeT_{ox}^{\bullet-}$ are in the ring-closed form with pK_a values of 5.2 and 2.4, respectively [2]. The radical cations are oxidizing species; electrode potentials of 1.4, 1.2, 1.1 V for $DTT_{ox}^{\bullet+}/DTT_{ox}$, $SeTT_{ox}^{\bullet+}/SeTT_{ox}$ and $DSeT_{ox}^{\bullet+}/DSeT_{ox}$, respectively, were determined with cyclovoltametry.

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Structural and Thermodynamic Study of Lanthanide Complexes with Planar Tridentate Ligands

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The complexation of trivalent lanthanide ions with tridentate aromatic ligand based on 2,6-bis(benzimidazol-2-yl)pyridine (L) is analyzed by using a combination of the *bond valence* method (for exploring solid state structures) with the thermodynamic *site binding* model (for unravelling coordination behaviour occurring in solution) [1].

Since a reliable set of bond valence parameters R_{ij} for Ln-O [2] and Ln-N [3] bonds involved in metal-organic complexes has been recently computed, we have performed bond valence sum analysis on single crystals structures for a series of complexes possessing different compositions (variable stoechiometries and counter-anions). Interestingly, the structural distortions evidenced by the *bond valence* method in the solid state are systematically correlated with anti-cooperative interligand interactions, which limits the stability of the complexes in solution. The stability and structures of lanthanide coordination complexes formed by the successive fixation of ligands, eventually leading to the triple-helical complexes $[LnL_3]^{3+}$, can be thus tuned by a judicious and predetermined choice of counter-anions and steric constraints.

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Luminescence and Photoredox Properties of Cyclometalated Iridium(III) Complexes

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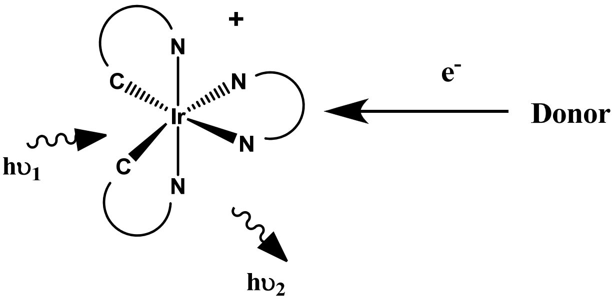
In the course of our research program on phototriggered long-range charge transfer [1][2], we investigate a series of cyclometalated iridium(III) complexes. Optical spectroscopic and electrochemical methods are used to explore the potential of these compounds as sensitizers for photoinduced electron transfer.



Toward this end, both *inter-* and *intra*molecular charge transfer reactions are studied.

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Synthesis, characterization and performance of supported gold catalysts in chemo-selective hydrogenation

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It was considered for a long time that gold is devoid of any catalytic activity. This had to be revised, since Haruta et al. established low temperature oxidation of carbon monoxide and Hutchings the synthesis of vinyl chloride via hydrochlorination of ethyne using gold. In contrast to previous reports on the poor activity of gold, these studies showed that gold was the best catalyst for these reactions [1]. The activity of gold is heavily dependent on its particle size. While bulk gold for instance is completely inactive, gold particles with a diameter less than 5 nm, dispersed on metal oxides are highly active for a number of reactions like for instance chemo-selective hydrogenation reactions [2]. Beside the particle size, alloying and the nature of the support greatly influence both activity and selectivity of supported metal catalysts. Goal of this work is to understand the origin of particle size and support effects on chemo-selective hydrogenation over gold catalysts. This will be achieved by combining precision synthesis of supported metal catalysts with kinetic measurements and in situ characterization. The reactivity of these catalysts is being studied for substrates containing various functional groups. To determine structure-performance relations, the preparation and the kinetic measurements are combined with in situ characterization methods based on X-ray spectroscopy. These enable to detect catalytically active sites and their interaction with reactants and intermediates under catalytically relevant conditions.

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Toward inert self-assembled d-block cryptates for trivalent lanthanides

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The stoichiometric mixing of the segmental ligand L (3eq) with $Ln(CF_3SO_3)_3$ (1eq) and $Cr(CF_3SO_3)_2$ (2 eq) followed by oxidation provides the bimetallic inert cryptate *HHH*-$[CrLnCrL_3]^{9+}$ (Ln=La-Lu).[1] The X-ray crystal structure of $[CrEuCrL_3]^{9+}$ confirms the formation of a trinuclear triple helix, in which the metals are regularly spaced by c.a. 9 Å, while NMR data collected on the analogous complex $[ZnEuZnL_3]^{9+}$ indicates that the wrapped structure is maintained in acetonitrile. Photophysical data demonstrate the operation of intramolecular intermetallic $Ln^{III}\leftrightarrow Cr^{III}$ energy transfer whose magnitude and direction can be tuned by a judicious choice of the central lanthanide cation. Reaction of $[CrEuCrL_3]^{9+}$ with strong donor for trivalent lanthanides (water, DMSO, DMF, fluoride) selectively produces the kinetically inert receptor *HHH*-$[Cr_2L_3]^{9+}$, which is highly preorganized for further lanthanide re-complexation.

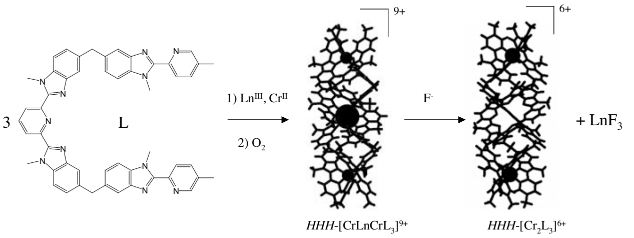

Figure 1: Self-assembly with post-modification of *HHH*-$[CrLnCrL_3]^{9+}$ followed by selective decomplexation of the central lanthanide.

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Fabrication of nano-sized $La(M,Pd)O_3$ (M= Mn, Fe, Co) perovskite type catalysts using ultrasonic spray combustion (USC)

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Ultrasonic spray combustion (USC) [1] has been used to synthesize in a one-step process nano-sized perovskite type oxides of formula $LaMO_3$ (M= Mn, Fe, Co). A series of process parameters (addition of citric acid (CA) to nitrate precursor solution, temperature of synthesis (Ts), post-calcination (Tc)) have been varied in the production of $LaMnO_3$ in order to define optimal synthesis conditions. The catalytic properties of the produced nano-sized materials have been probed using methane combustion as a test reaction ($O_2/CH_4=4$). The parameter study indicated that addition of citric acid is a pre-requisite to prepare $LaMnO_3$ with particles size of ca. 50 nm. Moreover, post-calcination is required to burn uncombusted precursors (nitrates) and to obtain defined crystalline phases. Catalytic activity decreased with increasing post-calcination temperature and with increasing CA concentration. Optimal conditions have been obtained with Ts=Tc=800°C and with a CA-to-metal ions ratio of 2.

Identical synthesis conditions can be used for $LaFeO_3$ and $LaCoO_3$ although parameters could be better adjusted for each single phase. Activity decreases in the order Mn>Co>Fe in agreement with reported trends [2].

The synthesis has been extended to Pd-containing perovskite type oxides (Mn and Fe) which are potential catalysts for stationary and automotive applications. Structural analysis by XANES revealed that Pd has been incorporated in a one step process within the perovskite structure.

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Thermoelectric Properties of $CaMn_{1-x}Nb_xO_3$

(x=0.01; 0.03; 0.05; 0.07; 0.10)

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Perovskite-type $CaMn_{1-x}Nb_xO_3$ (x = 0.01; 0.03; 0.05; 0.07; 0.10) phases were synthesized by a soft chemistry method. Results from a previous work have shown that $CaMn_{1-x}Nb_xO_3$ (x = 0.02) has the highest ZT_{1060K}= 0.32 if compared to x = 0.05 and x = 0.08 [1]. The focus of this work is on improving the ZT $_{1060K}$ by a finer variation of the Nb concentration in perovskite-type $CaMnO_3$. The crystallographic structures of the synthesised phases were obtained from x-ray powder diffraction data. The Seebeck coefficient and electrical resistivity were measured at high temperature using a RZ2001i equipment. The thermal conductivity of the dense ceramic samples was measured by combining Laser Flash Analysis and Differential Scanning Calorimetry. The highest Seebeck coefficient was reached for $CaMn_1.xNb_xO_3$ $(x = 0.01)_{1060K}$, the highest PF value for $CaMn_{1-x}Nb_xO_3$ $(x = 0.10)_{1060K}$., while $CaMn_{1-x}$ Nb_xO_3 $(x = 0.03)_{1060K}$ show the highest value of ZT= 0.17.

[1] L. Bocher, M. H. Aguirre, D. Logvinovich, A. Shkabko, R. Robert, M. Trottmann, A. Weidenkaff, *Inorg.Chem*, **2008**,*47 (18)*,8077.

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Soluble Gold Nanoparticles for Selective Hydrogenation of C=O Bonds

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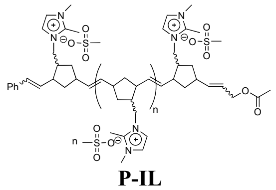
Transition metal nanoparticles (TM-NPs) are excellent candidates for performing a variety of catalytic applications. The primary advantages are high efficiency, recyclability and regioselectivity rivaling that of homogeneous processes, but operating under conditions for heterogeneous processes. However, the extremely small size associated with highly active TM-NPs (usually below 10 nm) require the use of stabilizers to prevent aggregation and catalytic deactivation.[1] In this project, a new class of stabilizers, a hybrid ionic polymer, was designed and synthesized through ROMP. The branches of this polymer incorporate an ionic liquid component (P-IL) allowing the modulation of the solubility properties by anion exchange. This P-IL was employed in the preparation of approximately 2 nm gold NPs which were characterized using UV-VIS and HR-TEM. The complete system was utilized for selective hydrogenation of α,β-unsaturated carbonylic compounds relevant in pharmaceutical and other industrial applications.



P-IL

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Modified Vitamin B$_{12}$ for Applications in Medicinal Chemistry

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Cobalamines are among the most important biomolecules that modulate their chemical and biological properties by the ability to switch between different coordination and conformational states.[1,2]
Based on this ability, we are interested in the design of corrin derivatives with novel functions.

We suggest a new strategy for the development of inhibitors of the enzyme methionine synthase based on B$_{12}$-hybrid derivatives: As a consequence of chemical modifications, the "base on/base off" equilibrium is disturbed and inhibition is expected while the analogue is still being transported into the cells.

We will present the synthesis and the spectrochemical properties of novel linker and ring modified corrin derivatives.

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Olefin Cyclopropanation via Sequential Atom Transfer Radical Addition – Dechlorination Reactions

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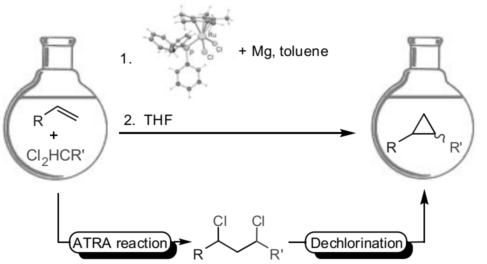
In organic synthesis, cyclopropanation reactions are often performed with Simmons-Smith-type reagents or by transition metal catalyzed reactions of olefins with diazo compounds[1]. We hereby describe a novel method for the synthesis of substituted cyclopropanes.



Olefins are reacted with 1,1'-dichlorides in a Ru-catalyzed atom transfer radical addition (ATRA) process[2] and the resulting 1,3-dichlorides are directly converted into cyclopropanes by reductive coupling with magnesium. This one-pot reaction is applicable to a variety of substrates and can be performed in an inter – or intramolecular fashion.

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[2] K. Thommes, B. Icli, R. Scopelliti, K. Severin, *Chem. Eur. J.* **2007**, *13*, 6899 - 6907

200

Microwave-assisted synthesis of mixed $ZnGa_2O_4$ nanomaterials

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The development of functional oxidic nanomaterials is a challenging field in modern materials chemistry, generating new compounds with interesting properties and a high application potential.[1] Thus, the synthesis and characterization of ternary oxides, such as $ZnGa_2O_4$, is in the focus of our research. This transparent and conductive spinel-type oxide emits blue light[2] and it is well known as a good low-voltage phosphor material and catalyst.[3, 4] The tetrahedral and octahedral sites in $ZnGa_2O_4$ were partially substituted - mostly via solid-state reaction, sol-gel, thermal evaporation or hydrothermal reactions - to bring forward new materials.[5] These mixed zinc gallates are used in image intensifiers or plasma display panels.[6] We now explore the microwave-assisted synthesis of $ZnGa_2O_4$ doped with paramagnetic transition metal and lanthanoid ions. This technique may replace standard hydrothermal methods due to its high efficiency, time-saving realisation, production of homogenous materials and moreover it shows better crystallisation kinetics. We investigated the morphology, chemical composition, photochemical properties and paramagnetic behaviour of microwave-synthesized doped $ZnGa_2O_4$ spinel particles. In particular, we focus on the (Zn, Cu)Ga_2O_4 systems that display a challenging structural chemistry and open up new ways to nanoscale Cu-catalysts in an interesting oxide matrix.

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Hierarchical Bi_2WO_6/TiO_2 Nanocomposites for Photocatalysis

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Bi_2WO_6 with a band gap of 2.7 eV is an important Aurivillius-type oxide consisting of characteristic perovskite-like layers of $[WO_4]_n^{2-}$ and $[Bi_2O_2]^{2+}$. Recently, hydrothermal syntheses of hierarchical Bi_2WO_6 microspheres have been reported which displayed high photocatalytic activities in the decomposition of organic dyes under visible light-irradiation [1-2].

On the other hand, TiO_2 is still the industrial standard for photocatalysis. However, it is only activated by UV irradiation, thereby utilizing only a small fraction of solar light. One of the most promising ideas to enhance the absorption spectrum of TiO_2 is its coupling with narrow band gap semiconductors [3].

Here, we present a simple, novel, and efficient low-temperature route to fully coat hierarchical hydrothermally synthesized Bi_2WO_6 microspheres with anatase TiO_2 nanopartices (diameters around 20-40 nm) (Figure 1) and we furthermore report on the photocatalytic activity of the composites.

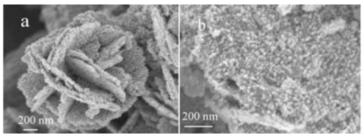

Figure 1. Representative SEM images of hierarchical Bi_2WO_6 microspheres after coating with TiO_2

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Synthesis of New Silver Compounds with derivates of nicotinate

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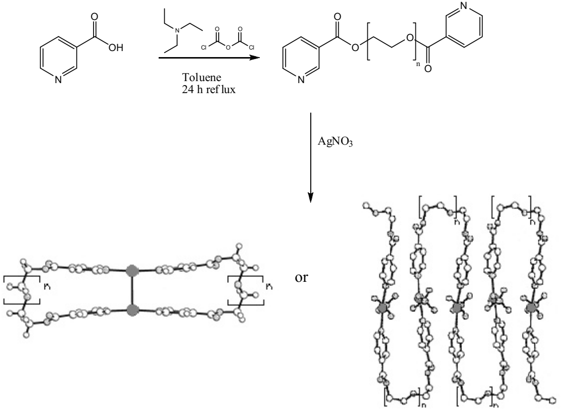
Silver ions have antibacterial properties, and complexes with this ion have a great potential of applications in medical uses. Complexes of silver with several ligands derived from nicotinic acid and with up to three ethylene oxide groups as spacer are already known. In our group, we obtain metallacycles, and under special conditions, chain structures. We propose the development of complexes with longer spacers and to study the possible formation of solids, liquid crystals or polymers.



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Kinetics of Reactions of Amino Acid Radicals with Ascorbate

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Proteins are important biological targets for partially reduced oxygen species *in vivo*. The amino acid radicals ($AA^\bullet$) formed in the process on the protein yield, in the presence of oxygen, peroxyl radicals ($AAOO^\bullet$). Both radical types can initiate deleterious reactions *in vivo*. We studied the *N*-acetylamide derivatives of selected amino acids as models of these residues in proteins. We generated amino acid radicals specifically by hydroxyl radicals produced in solutions irradiated with 2 MeV electrons in the presence of N_2O. In the absence of O_2, the amino acid radicals decayed with rate constants that varied between 10^8 to 10^9 $M^{-1}s^{-1}$. The disappearance of the radicals was followed at 250– 370 nm. In the presence of O_2, the amino acid radicals reacted rapidly to form the corresponding peroxyl radicals with rate constants of in the range $(1–5) \times 10^9$ $M^{-1}s^{-1}$, depending on the amino acid.

We have shown that ascorbate, the principal endogenous biological antioxidant, is able to repair tyrosyl and tryptophanyl radicals in various proteins.[1] The peroxyl radicals of all amino acids studied here were also repaired by oxidizing ascorbate to the ascorbyl radical. The reaction was followed at 360 nm, where ascorbyl radical has an absorption coefficient of 3300 $M^{-1}cm^{-1}$, and the rate constants were strongly dependent on the nature of the amino acid. It is to be stressed that repair of $AAOO^\bullet$ by ascorbate gives rise to hydroperoxides (AAOOH) that are also reactive molecules. Our study suggests that reaction with protein radicals may be responsible for the ascorbate loss reported in organisms exposed to oxidative stress.

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Nanostructured Chitinous Frameworks for Metal Ion Absorption

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Recently, chitin with the α-structural backbone has been found to be present in spongin fibres of Aplysina sp. and Verongula gigantea [1]. It is well known that fibre skeletons of marine sponges exhibit bioactive properties which can be exploited for biomedicinal applications [2]. We study the ability of the α-chitin - as skeletal frameworks derived from the verongid sponges - to absorb metal ions and to act as a vehicle for functional oxides. Our preliminary investigations have shown that the internal structure of the skeletal matrix displays a porous network (Figure 1) that is indeed capable of absorbing metal ions. We hope that these studies will enhance the application spectrum of chitin, particularly for detoxification purposes.

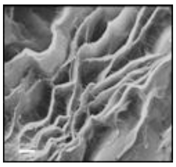

Figure 1. Representative SEM image of a skeletal chitinous framework (scale bar = 100 nm).

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NOVEL TYPE OF CHIRAL FERROCENYL TRIFLUOROMETHYLPHOSPHINES

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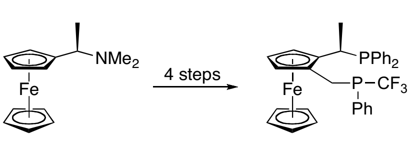
Chiral bidentate ferrocenyl ligands, such as *Josiphos*, constitute one of the most successful class of auxiliaries used in asymmetric catalysis as they are used in a number of industrial applications.[1]

New planar chiral trifluoromethylphosphine ferrocenyl ligands of type **1** (2 diastereomers) were prepared from Ugi's amine in four steps. Several complexes with late transition-metals have been prepared in order to study the coordination-chemical as well as steric and electronic properties of ligands **1**.



Ugi's amine

1

The selectivity, activity and productivity of theses complexes with chiral PPh_2-$PPh(CF_3)$ ligands **1** will be presented for different enantioselective catalysis.

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Polyoxometalates as Potential HIV Protease Inhibitors

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Polyoxometalates (POMs) are metal-oxygen nanoclusters that are usually formed by early transition metals in their high oxidation states (mainly Mo, W and V). The Keggin $[(PO_4)W_{12}O_{36}]^{3-}$ and Wells-Dawson $[P_2W_{18}O_{62}]^{6-}$ ions are probably the most prominent POM representatives. The exceptional structural versatility of POMs has attracted many scientists worldwide as well as their manifold applications and properties, e.g. their high antibacterial, antitumoral, antiviral and antiretroviral activity.[1] In addition, POMs can also interact with proteins and induce the selective precipitation of prions.[2] The first clinical trials with polyoxotungstates (HPA-23, (ammonium-21-tungsto-9-antimoniate) have been performed in the 1980s involving patients suffering from Acquired Immune Deficiency Syndrome (AIDS).[3] Starting from these insights, we have synthesized and purified HIV-1 protease as well as an arsenal of POMs covering a wide range of structure types and compositions, e.g. Gd-containing large polyoxotungstates with promising features as MRI contrast agents.[4] They are currently screened for their activity as HIV protease inhibitors, because preliminary studies indicated that they offer a new inhibition mode remote from the active site.[5] This might be an approach to tackle the ongoing problem of viral resistance.

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Development of Artificial Enzymes: A Computational Study

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By linking a catalytically active metal complex into a protein, it is possible to combine the activity of a metal with a chiral protein environment to generate an enantioselective artificial metalloenzyme [1;2]. A requirement for such an artificial enzyme is a deep binding pocket to allow catalysis, with a stable connection between the two building blocks. In the past, we have relied on the biotin-avidin technology to anchor the metal moiety within a protein environment. Although the resulting hybrid catalysts proved efficient for a variety of transformations, both computational and structural characterization suggested that the metal moiety was delocalized in a shallow potential energy surface. This makes the rational optimization of such systems difficult, as the chiral environment responsible for enantioselection is poorly defined. To overcome this limitation, docking experiments and molecular dynamics simulations are performed to devise and optimize combinations of mutations near the cavity and different linkers, to create better defined and more efficient artificial metalloenzymes.

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Ionic phosphites for palladium catalyzed Suzuki C-C coupling reactions in ionic liquids

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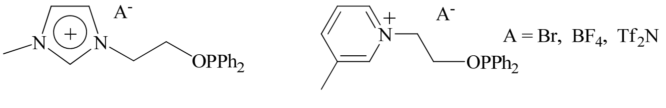
Phosphites are widely used as ligands in catalysis. Numerous neutral phosphites have been prepared whereas relatively few ionic phosphites are known.[1] We have prepared a series of ionic phosphites and used them as ligands in combination with $PdCl_2$ for Suzuki C-C coupling reactions in ILs as reaction media. [2]



Remarkable improvements were obtained with the yield of the biphenyl can be reached as high as 95% for iodobenzene or bromobenzene after 4 h at 110°C. The improvement is even more significant for sterically hindered or deactivated aryl halides under mild conditions.

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Reactivity of an Antimetastatic Organometallic Ruthenium Compound with Metallothionein-2: Relevance to the Mechanism of Action.

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Following the discovery of the anticancer properties of cisplatin in 1965,[1] many inorganic and organometallic compounds have now been evaluated for anticancer activity. In recent years, we have developed of a family of ruthenium(II)-arene complexes showing antimetastatic properties.[2]
Unlike cisplatin, which exhibits its main chemotherapeutic action through binding to the bases of DNA, the mechanism of action of the Ru(II) compounds may involve interactions with critical intracellular proteins. Overall, for metal-based drugs it is of interest to characterize their interactions with proteins that might constitute intracellular targets and that might be responsible for the mechanisms of pharmacological action of this class of compounds. Within this frame, the protein superfamily of cysteine- and ZnII-rich proteins metallothioneins (MT) account for the intrinsic and acquired resistance of platinum drugs because of the strong reactivity of platinum compounds with S-donor molecules.
In the present study the reactions of MT-2 with the representative anticancer compound [Ru(η^6-p-cymene)Cl_2(pta)], termed RAPTA-C, were investigated through ESI-MS. The studies were performed in comparison to cisplatin. Remarkably, important differences in the binding of the two complexes to MT-2 have been observed. The mechanistic implications of these results are discussed.

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Comparison of ligand bonding in rhodium porphyrin complexes

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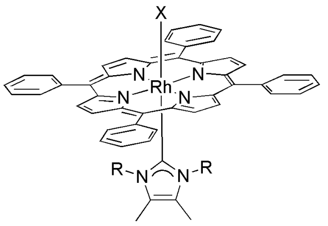
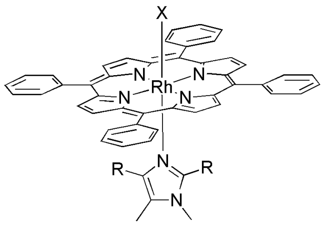
Porphyrin complexes are biologically important structures and models are often used for preparing bio-inspired catalysts. Rhodium porphyrins bearing different apical ligands have been widely studied for their broad catalytic activity [1].
We have synthesized rhodium *meso*-tetraphenylporphyrin complexes bearing either an imidazole or an N-heterocyclic carbene ligand in order to compare their impact on structure and activity. In such complexes, the high *trans* effect of NHCs can be exploited. We will present our progress in studying effects arising from the introduction of different types of ligands with similar steric demands and from changing the wingtip groups R on the NHC ligand.





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Carbon Dioxide as Hydrogen Vector - Hydrogen Generation from Formic Acid: Advantages of Ionic Liquids as Reaction Media

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Hydrogen is a valuable industrial material and most probably it will be the future energy carrier. The widespread application of hydrogen is currently limited mainly because of storage and delivery problems. Formic acid is one of several hydrogen sources, it has a number of advantages including a high flash point (+ 69 °C), high volumetric hydrogen density (53 g/L), etc. A new, viable method[1,2] has been reported recently for hydrogen production from formic acid using a homogeneous catalysts system in aqueous solution. Ionic liquids (ILs) have extremely low volatility, high thermal stability, and strong solvating power for various substances, they are often regarded as "designer solvents" with tunable properties. ILs can be used not only as solvents and for immobilizing catalysts for HCOOH decomposition, but as the H_2 and CO_2 solubilities in ILs are very different,[3,4] ILs can play an important role in the gas mixture separation.
We will present our results using ILs as reaction media for hydrogen production from acid formic.

Acknowledgment. The Swiss National Science Foundation and EPFL are thanked for financial support.

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Biological Ferric Citrate: Fenton or Phantom?

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Ascorbate is generally regarded to be responsible for the reduction of iron(III) in low molecular weight non-transferrin bound iron (NTBI), and the widely held consensus is that iron-citrate complexes reduce hydrogen peroxide and are therefore the source of hydroxyl radical generation *in vivo*. While being known for over thirty years [1], the ascorbate induced Fenton reaction of ferric citrate complexes has not been investigate to date. We've investigated the reduction of ferric citrate complexes under physiological conditions; ($[Fe]_{final}$=50 M and Fe:Citrate ratios 1:10 and 1:100) with biological reductants and cyclic voltammetry. Our observations from stopped flow experiments have shown that ascorbate, dithiothreitol (DTT) and NADPH reduce iron(III) slowly at pH 7.4 and as a result, the iron does not redox-cycle at a rate commensurate with the progress of oxidative damage. Since ascorbate was unable to reduce iron-citrate, we assumed that the reduction process may be enzyme-assisted and tried to effect iron reduction using duodenal cytochrome b_{561}(Dcytb_{561}). Although we observed a limited increase in the rate of ascorbate induced iron reduction in the presence of Dcytb_{561}, it was too slow to be of biological relevance. This is in agreement with the data obtained from cyclic voltammetry, which showed that iron citrate complexes are redox inactive. The oxidation of Fe(II) citrate by H_2O_2 is a slow reaction, and cannot compete with the reaction of H_2O_2 with catalase. Our data clearly shows that the iron-citrate complexes are not directly responsible for hydroxyl radical generation *in vivo*, and that NTBI is an innocent symptom of excess iron.

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Abnormal 1,2,3-triazolylidene complexes : synthesis, electronic, and catalytic properties

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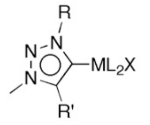
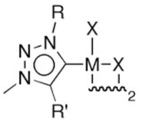
Abnormal N-heterocyclic carbenes (NHCs) have emerged as very powerful ligands in catalysis, predominantly due to their stronger σ-donation as compared to normally bound NHCs.[1] While most often abnormal NHCs are derived from imidazolium salts, new classes have been developed.[2] We have recently used 1,2,3-triazolium salts as versatile precursors for abnormal NHCs.[3] Different metals like Ru, Rh, Ir, and Pd can be installed either by transmetallation or via direct metallation to generate monometallic or dimetallic complexes (see figure).





We have now synthesized complexes containing triazolium-derived NHCs with different wingtip groups R and R' (alkyl or aryl). We will present our investigations on rhodium complexation, which allowed us to determine the direct electronic influence of the wingtip group on the metal center. We will also discuss the potential catalytic activity of these new complexes.

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New Rhenium Complexes With Chiral Ferrocenyl Ligands

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In the last twenty years, there has been an increasing development of transition metal-catalyzed organic reactions using rhenium-based catalysts and ligands [1]. These reactions include among others C-C, C-N, C-O, C-S and C-Si bond formations. However, there are only few reports of enentioselective rhenium-catalyzed reactions [2].

We synthesized and characterized a series of novel rhenium complexes containing chiral ferrocenyl ligands of the Josiphos [3] and Pigiphos [4] families. All the complexes were synthesized starting from commercially available rhenium precursors and showed to be air and moisture stable in various oxidation states (I, III and V) and with different accompanying ligands such as, halides, hydrides, oxygen and CO. To the best of our knowledge, these complexes are the first examples of chiral rhenium compounds with non-C_2 symmetric ligands. Ther catalytical behaviour is currently under study.

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Alkyne and Arene Hydrogenation by Immobilized Pd and Rh Nanocatalysts Stabilized by Imidazolium Functionalized Bipyridine Derivatives

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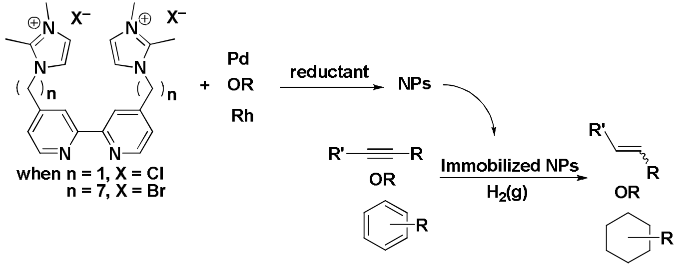
2,2'-Bipyridine (bipy) and analogous compounds have been used to stabilize both Pd and Rh nanoparticles. With PdNPs, phenanthroline has been shown to promote high selectivity in the partial hydrogenation of both dienes and alkynes and as a stabilizer/additive for the biphasic hydrogenation of various alkenes in ionic liquids [1]. With RhNPs, bipy was employed as a stabilizer in the complete reduction of aromatic compounds [2]. Based on this research, we synthesized two imidazolium tagged bipyridine compounds (Figure) to promote retention of the NPs on either oxidized carbon nanofiber supports (PdNPs) or in an ionic liquid (RhNPs). The stabilizer and subsequent nanoparticle synthesis and catalytic results for the hydrogenation of alkynes and arenes will be presented.



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Self Replication *via* Thiol/Disulfide – Copper(I)/(II) Redox in Thiol Substituted 2,2'-Bipyridine and 2,2':6',2"-Terpyridine Complexes.

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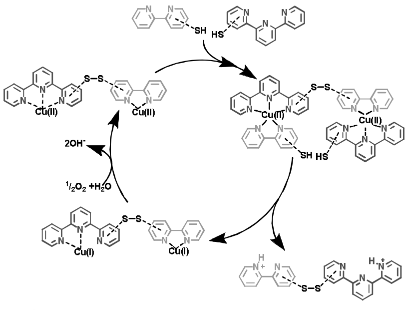
We are interested in utilising the precepts of metallosupramolecular chemistry for the development of self-replicating systems.[1] Our approach is predicated upon the following: (i) preference of Cu(II) for 5-coordinate {Cu(tpy)(bpy)} environments[2] (ii) reversible metal-mediated oxidative coupling reaction of thiols to disulfides[3] (iii) on reduction, Cu(I) will not stabilise a 5-coordinate complex, releasing the newly formed ligand and (iv) the exposed Cu(I) cation will be readily oxidized by oxygen to regenerate the Cu(II).



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The origin of catalytic activity of a nonporous Cu-MOF possessing saturated metal sites

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Metal-organic frameworks (MOFs) have received increasing attention as new promising materials for gas storage, separation, and catalysis. $Cu(bpy)(H_2O)_2(BF_4)_2(bpy)$ (Cu-MOF, bpy: 4,4-bipyridine) [1], with hydrogen-bonding regulated flexible framework that has no open pores in the original structure, is an extremely interesting recyclable catalyst with high catalytic activity in the ring-opening of epoxides with MeOH [2]. Herein, the nature of active sites of Cu-MOF in MeOH was investigated by ATR-IR, Raman, EPR, and UV-vis spectroscopic techniques. Cu-MOF has highly dynamic structural properties responding to MeOH, restructuring its framework dimension from 3D to 2D by forming a highly symmetric coordination of four bpy units to Cu. This interaction resulted in the partial dissolution of Cu-MOF as multi-Cu complexes, in which Cu^{2+} ions are connected with bpy ligands. Both dissolved Cu-MOF in the liquid phase and restructured 2D Cu-MOF in the solid phase were catalytically active, the former being more active than the latter. Finally, addition of ethyl ether into the reaction mixture induced the reconstruction of both dissolved and solid Cu-MOF into the original framework structure, allowing excellent recyclability of Cu-MOF as an apparent heterogeneous catalyst.

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Ruthenium Based Models for Photoinduced Proton-Coupled Electron Transfer

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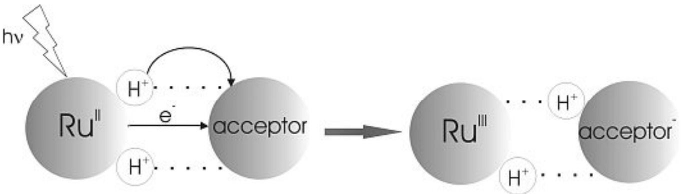
Following up on our recent studies of iridium (III) based systems [1], we are now exploring ruthenium (II) based models for proton-coupled electron transfer.



Our targets are hydrogen-bonded donor-acceptor systems in which the overall reaction can be triggered by light.

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Investigation of Phosphate Binding with Benzimidazole-based Cations

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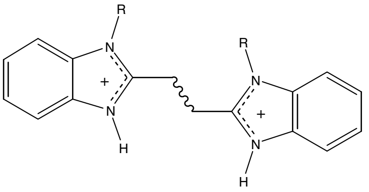
Phosphates are commonly occurring biologically relevant anions and environmentally important for water quality monitoring and control [1-3]. Benzimidazole cations and $H_2PO_4^-$ anions have comparable pK_a values and hence, from the equalisation principle [4], should interact favourably together and exhibit strong hydrogen bonding.

In the solid state the protonated ligand **L** (R = H, Me) forms a salt $\mathbf{L}H_2^{2+}(H_2PO_4^-)_2$ in which the protonated ligand hydrogen bonds strongly to infinite hydrogen bonded $\{(OH)_2PO_2^-\}_n$ chains.



L

Potentiometric titrations, in 50/50 methanol/water, confirmed binding in solution. The speciation diagram shows that between pH values of 3 and 9 more than 50% phosphate is bound to the ligand. The investigation also included the binding of arsenate and sulphate ions.

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The Kinetics of Metal Exchange in Dinuclear Triple Helicates

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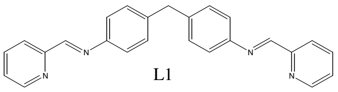
By definition the lability of the metal-nitrogen coordinate bond enables metal exchange to occur even in systems as complex as helicates. Such an exchange was examined for two triple-helicate systems. One of the systems contains a pyridylimine ligand L1 [1], where the CH=N bond may be labile [2], while the second system has a stable ligand, a bis-(isoquinoline-benzimidazole) L2. Both ligands form dinuclear triple-stranded helicates in the presence of an octahedral metal ion but the kinetics of metal exchange revealed a different mechanism for each system. This poster will present recent advances in studying the kinetics of metal exchange and the relative stability of the helicates when using different *3d* metal ions.



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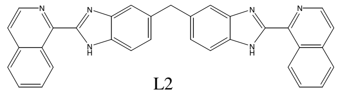

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Mercury-Containing RNA Scaffolds

Susann Paulus[1], Silke Johannsen[1], Nicole Düpre[2], Peter W. Thulstrup[3], Lars Hemmingsen[3], Jens Müller[2], Roland K.O. Sigel[1]

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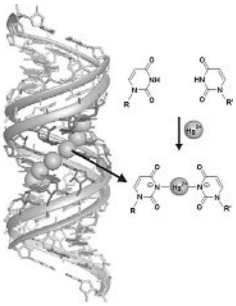

Metal ion-mediated base pairs in nucleic acids become increasingly important for potential applications like molecular wires.[1] Using *in vitro* transcription we synthesized single-stranded RNA containing continuous stretches of uracil in high yield. In the presence of Hg^{2+} the RNA rearranges from a hairpin containing mismatched U-U pairs to a more stable duplex by forming U-Hg^{2+}-U base pairs. This structural conversion and the final RNA-Hg^{2+} scaffolds were characterized by NMR, DLS, UV and CD spectroscopy.[2] To investigate the U-Hg^{2+}-U coordination environment we used ^{199m}Hg perturbed angular correlation of γ-rays (PAC) spectroscopy. This represents the first application of PAC spectroscopy to elucidate the local electronic and molecular structure of metalated nucleic acids.

Financial support by ERAnet-Chemistry, the *Deutsche Forschungsgemeinschaft*, the Swiss National Science Foundation, within the COST D39 Action, and the beam time grant IS448 from CERN/ISOLDE is gratefully acknowledged.

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Interaction of Peroxynitrite with Buffers

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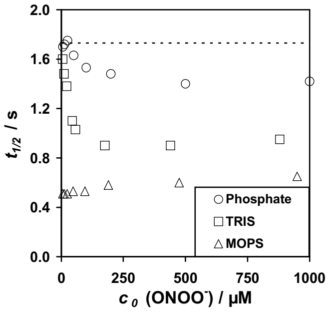
Peroxynitrite is of biological interest since it can be formed by the rapid recombination of superoxide and nitrogen monoxide [1], both present in living organisms. Biochemical experiments are usually carried out in buffers which are assumed to be inert except for proton transfer.

We show that typical biochemical buffers react with peroxynitrite: phosphate, tris-(hydroxymethylaminomethane) (TRIS) and 3-(N-morpholino) propanesulfonate (MOPS). The dominant reactions depend on the buffer type and the peroxynitrite concentration. They occur at pH values near the pK_a=6.8 of peroxynitrous acid [2]. Telltales of the buffer reactions are concentration dependent kinetics aberrations from predicted values of peroxynitrite isomerization (dashed line in figure) or formation of colored products in case of MOPS. Some of the products could be identified.



The kinetics deviations suggest that reliable results can be obtained for peroxynitrite reactions in phosphate and TRIS buffers at sufficient dilution; the common *bolus* addition of high peroxynitrite concentrations will lead to errors. MOPS and structurally related buffer materials cannot be used at all. The figure shows the half-life of peroxynitrite in the buffers, dependent on initial concentration, at pH = 7.

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Ionic Strength Dependence of Cu,Zn-Superoxide Dismutase Activity

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Electrostatic interactions play an important role in a variety of biological processes, e.g., the electrostatic potential surface of a protein, as well as its function and reactivity, can be significantly affected by ionic strength. The ionic strength dependence of the activity of Cu,Zn-superoxide dismutase (Cu,Zn-SOD), a family of enzymes that catalyze the disproportionation of the superoxide radical, has been studied for several decades. Early studies by Rigo et al. [1] showed that the activity of the Cu,Zn-SOD decreases with increasing ionic strength; McAdam [2] reported a similar dependence at high ionic strength, but found that the activity remains constant at ionic strengths less than 0.1 M. In our previous investigations of the ionic strength dependence of Cu,Zn-SOD activity by pulse radiolysis [3], we found evidence that both native enzyme and holo Cu,Zn-SOD reconstituted from metal-free enzyme show a positive dependence of activity on ionic strength up to ca. 15 mM. Models of the ionic strength dependence of the activity of Cu,Zn-SOD predict that the rate constant for dismutation initially increases at low ionic strength and then decreases at moderate to high ionic strength [4]. We examine the ionic strength dependence of the Cu,Zn-SOD reaction under conditions of ultra-low ionic strength and compare our findings with computational models.

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Improving Activity, Stability and Selectivity of Artificial Enzymes Based on the Streptavidin-Biotin Technology

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Metal-catalyzed enantioselective transformations are recognized among the most efficient ways to produce enantiomerically pure compounds.

Based on the incorporation of biotinylated metal complexes within (strept)avidin as host protein, we have obtained efficient artificial metalloenzymes for enantioselective reactions including hydrogenation of *N*-protected dehydroaminoacids [1, 2] and allylic alkylation[3].

Chemical and genetic optimizations afford artificial metalloenzymes with good selectivities (up to 95% ee) and good tolerance to organic solvents.

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Structural investigation and metal ion titration of a bacterial group II intron catalytic core

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Group II introns are among the largest natural ribozymes and able to catalyze their own excision from RNA as well as their reinsertion back into RNA or DNA. These RNAs consist of five domains which fold to a compact tertiary structure upon addition of Mg^{2+} [1,2]. Situated in the catalytic core is the highly conserved domain 5, a 34-35nt long hairpin comprising many nucleotides involved in catalysis or contacts to other intron domains [3]. Currently there are structures of three different domains 5 available [4]. *Azotobacter vinelandii*'s A.v.I5 is an intron of type IIb whose domain 5 contains an unusual nucleotide sequence in the highly conserved region known as the 'catalytic triad' as well as a pentaloop [5]. By solution NMR we are characterizing the impact of these features on the structure as well as the metal ion binding properties of the domain.

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

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Triangular Trinuclear Assembly: Luminescent Box in Water

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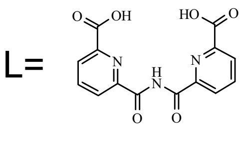
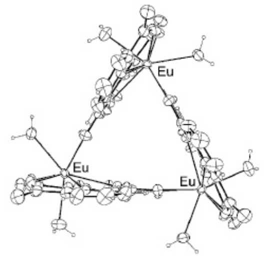
A number of multidentate receptors were prepared in the past in order to develop stable Ln(III) luminescent and paramagnetic devices. Herein we report on the synthesis of a new ligand **L**, which has been designed for Ln(III) coordination by coupling two 2,6-dicarbonylpyridine subunits [1].





The self-assembly of this receptor with lanthanide cations results in the formation of discrete trinuclear complexes: **$[(L\text{-}3H)_3Ln_3]\cdot 6H_2O$**[1]. X-ray crystallography shows that three nine-coordinated cations are interlinked by ligands to provide triangular complexes. This peculiar structure is maintained in solution, as it is shown by NMR and photophysical studies. Despite two water molecules coordinated to each europium cation, these topologically unusual complexes exhibit remarkable luminescent and paramagnetic properties and make them excellent candidates for bimodal imaging.

[1] S. Zebret, N. Dupont, G. Bernardinelli, J. Hamacek, *Chem. Eur. J.* **2009**, *15*, 3355.

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Structural and kinetic investigations for the labeling of biomolecules with the $\{TcO_3\}$-core

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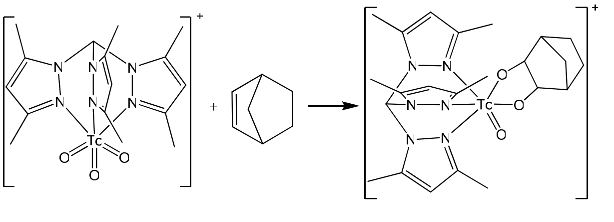
The radio isotop ^{99m}Tc has excellent nuclear properties for radiopharmaceutical applications. In this context, complexes containing the $\{^{99(m)}TcO_3\}^+$-core are of high interest for the development of a new strategy for the labeling of biomolecules by a [3+2] cycloaddition with alkenes.[1, 2]



Model complexes $[TcO_3(L)]^+$ (L = 1,4,7-triazonane, 1-benzyl-1,4,7-triazonane and tris(3,5-dimethyl-1H-pyrazol-1-yl)methane)) and their diolato derivatives $[TcO_3(L)(eg\text{-}R)]^+$ were synthesized and characterized. Furthermore, the reaction mechanism of the [3+2] cycloaddition was investigated by kinetic measurements. The kinetic data indicate, that the reaction has associative driven mechanism and the rate constant k_1 strongly depends on the type of the alkene.(k_1=0.005 to 46 $M^{-1}S^{-1}$).

The results will help to optimize the reaction conditions and to find an appropriate alkene to make this new labeling approach competitive with today used labeling techniques.

[1] Y. Tooyama, H. Braband, B. Spingler, U. Abram, R. Alberto, *Inorg. Chem.* **2008**, *47*, 257-264.

[2] H. Braband, Y. Tooyama, T. Fox, R. Alberto, *Chem. Eur. J.* **2009**, *15*, 633-638.

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A Viable Hydrogen-Storage System Based On Selective Formic Acid Decomposition With Homogeneous and Heterogeneous Ruthenium Catalysts

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No ideal solution for hydrogen storage and delivery exists, limiting the possibility of a worldwide hydrogen economy. A viable system, based on the selective homogeneous catalytic decomposition of formic acid into H_2 and CO_2, in a wide pressure range, has been proposed recently.[1,2]

Table 1. Volumetric hydrogen densities for different storage systems.

Storage	Pressure	Temperature	H "density"
hydrogen gas	350 bar	25 °C	28 g/L
liquid hydrogen	1 bar	- 253 °C	70^a g/L
formic acid	1 bar	25 °C	53 g/L

[a] about 20 % of H_2 is lost to cool down/liquefy

The catalytically active species are formed *in situ* from $RuCl_3$ and TPPTS in the liquid phase, in aqueous solution.[3] The utility of liquid catalyst/solutions are limited in the case of mobile, portable applications.

We will present our results concerning the immobilization/solidification of the catalysts for hydrogen production from acid formic.

Acknowledgment. The Swiss National Science Foundation and EPFL are thanked for financial support.

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[2] C. Fellay, P. J. Dyson, G. Laurenczy, *Angew. Chem. Int. Ed.*, **2008**, *47*, 3966.

[3] C. Fellay, N. Yan, P. J. Dyson, G. Laurenczy, *Chem. Eur. J.*, **2009**, *15,* 3752.

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Chain scission mechanisms in a polymer electrolyte fuel cell membrane

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The proton exchange membrane is a key component of the polymer electrolyte fuel cell (PEFC). In the current stage of technology, perfluorinated membranes are the materials of choice in many applications. However, given the cost of these membranes, a range of alternative membrane technologies are under investigation. Optimized radiation grafted membranes on the basis of styrene and α-methylstyrene show comparable performance to perfluorinated membranes. In order to improve the current durability of several thousands hours at practical operating conditions [1], we examine the mechanism of the degradation.

The chemical degradation is affected by several experimental parameters, including effect of external load, reactant gas and relative humidity. Gas-crossover (H_2, O_2) through the membrane apparently correlates with membrane degradation. Evidence of $HO^{\bullet}$ formation in a fuel cell has been obtained recently [2]. On the basis of pulse radiolysis experiments with an oligomer of poly(sodium styrene sulfonate) in the presence of O_2, we propose a detailed mechanism that starts with hydroxyl radical addition to the aromatic ring and concomitant benzylic hydrogen abstraction, followed by addition of dioxygen to the benzylic radical. In combination with standard reduction potentials of couples with relevance for the fuel cell membrane, we propose a chain scission mechanism. The elucidation of weak points in the polymer membrane might serve as a basis for further membrane improvement.

[1] Gubler L., Kuhn H., Schmidt T.J., Scherer G.G., Brack H..P and Simbeck K., *Fuel Cells* **2004**, *3*, 196.

[2] Ohguri N., Nosaka A.Y., Nosaka Y., *Electrochemical and Solid State Letters*, **2009**, *12*, B94.

230

Gold Nanoparticles Functionalized with Gadolinium Chelates as High Relaxivity MRI Contrast Agents

L. Moriggi, C. Cannizzo, A. Ulianov, E. Dumas, C. R. Mayer and L. Helm

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We developed small, stable, water-dispersible, DTTA[1] thiol functionalized gold nanoparticles (DtNP) complexed with paramagnetic gadolinium or diamagnetic yttrium rare earth ions (Gd-DtNP and Y-DtNP).

Characterizations using TEM images, dynamic light scattering technique and STEM with EDX analysis indicate a particle size distribution from 2-15 nm. Molecular modelling shows a thickness of the coating shell of roughly 1.3 nm as measured between the rare earth ions and the gold core surface.

Accurate Au and Gd or Y concentrations have been determined with ICP-MS technique. Bulk magnetic susceptibility measurements at high magnetic field of different concentrations of Gd-DtNP and Y-DtNP samples showed the absence of a significant magnetic contribution due to the gold core.

NMRD profiles of Gd-DtNP solutions at 25°C show very high relaxivities with marked relaxivity humps between 10 and 60 MHz indicating slow rotational motion. The "modified Florence approach"[2] fits well the experimental points of the NMRD profile of Gd-DtNP(1) even at high frequencies indicating that the nanoparticles behave as rigid units. The fitted parameters describing the electron spin relaxation are finally in good coherence with what was expected from the Ru-based metallostar values.[3]

[1] L. Moriggi, C. Cannizzo, C. Prestinari, F. Berrière, L. Helm, *Inorg. Chem.* **2008**, *47*, 8357.

[2] I. Bertini, O. Galas, C. Luchinat, G. Parigi, *J. Magn. Reson.* **1995**, *113A*, 151.

[3] L. Moriggi, A. Aebischer, C. Cannizzo, A. Sour, A. Borel, J. C. G. Bünzli, L. Helm, *Dalton Trans.* **2009**, 2088.

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Rational Design of Thermotropic Mesophases in Lanthanidomesogens

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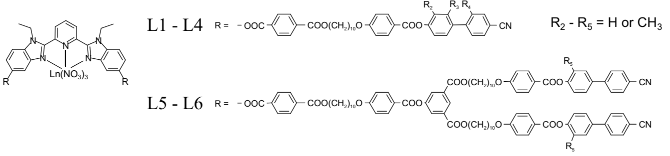
The combination of a tridentate coordination unit with different dendrimeric arms yields ligands that form complexes with lanthanide ions, which are potential candidates for forming liquid crystals.



The properties of the complexes have been investigated by means of DSC, POM and SAXS. Whereas complexes of the smaller **L1**-**L4** exhibit no mesogenic behaviour, complexes of the larger **L5** of general composition [Ln(**L5**)(NO_3)$_3$] form smectic phases over large temperatures with clearing temperatures around 186 - 200 °C. Introduction of methyl groups in **L6** leads to lower clearing temperatures (144 - 159 °C) as well as the formation of nematic phases in a narrow temperature domain. The influence of the methyl groups on the ordering in the mesophases is compared with thermodynamic parameters for the [Ln(**L**)(NO_3)$_3$] ⇆ [Ln(**L**)(NO_3)$_3$]$_2$ (**L** = **L1** - **L6**) dimerization process which has been studied in CD_2Cl_2 solution by variable temperature ^{1}H NMR.

[1] T. B. Jensen, E. Terazzi, B. Donnio, D. Guillon, C. Piguet *Chem. Commun.*, **2008**, 181-183.

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Copper(I) Complexes for Dye Sensitised Solar Cells and LEECs

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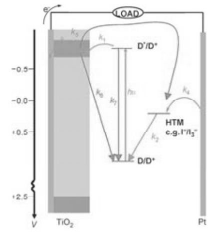
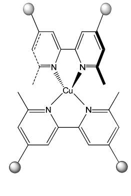


The sunlight can be converted into electrical energy. We are developing new models of solar cells and we are investigating their performance. Up to now, Cu(I) 2,2'-bipyridine complexes, used as sensitisers for dye sensitised solar cells (DSSCs), represent an interesting and cost-effective alternative to most efficient Ru (II) complexes used. The structure of the organic part of the complex can affect consequently the efficiency of the solar cells; therefore the structural modification of the ligands is well studied. Furthermore, there is a possible application of our Cu(I) complexes for LEECs, in competition with the OLEDs. Till now, ruthenium and iridium complexes are the most common systems used. Hence, it is possible to optimize the color and to increase the efficiency of the emitted light.



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Dinuclear tungsten butadiyne complexes based molecular wires

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Dinuclear metal complexes of the type $[L_nMC_nML_n]$ (M = Mn, Re, Ru, Fe, Pt) that are bridged by a linear, unsaturated carbon chain are of exceptional interest as building blocks for molecular electronics.[1] Reversible oxidations, strong communication between metal centres, chemical and thermal stability are required from molecules, which could be potentially applied in electronic devices. To combine these properties in target molecules, tungsten-based organometallic molecular wires were designed. Tungsten compounds offer facile oxidation state switching by forming relative stable cumulenic and carbyne species,[2] making them ideal candidates for molecular wires.

Currently complexes $[L_nMC_nML_n]$ (M = W) of this type remains poorly investigated and only a few of them are structurally characterized.[3] Here, we present a new and straightforward synthesis of tungsten complexes with the general formula: $[W(CO)_2(dppe)(X)]_2\mu\text{-}C_4$ (X = Cl, I). These compounds show fac-geometry on the metal centres and have a bond length distribution in the WC_4W bridge that resembles close to a carbyne type structure. Synthetic methods were developed for substitution of two or four CO molecules and halogen substitution.

All complexes were characterized by single crystal X-ray structure analysis, ^1H, ^{13}C, ^{31}P NMR, IR, RAMAN and UV-Vis spectroscopy. Interaction between tungsten centres was investigated by: Cyclic voltammetry (CV), EPR, IR, Near-IR and magnetization measurements. Physical studies of the complexes revealed that the $[W{\equiv}C\text{-}C{\equiv}C\text{-}C{\equiv}W]$ system belongs to class of moderately interacting systems.

[1] Roberts, R. L.; Puschmann, H.; Howard, J. A. K.; Yamamoto, J. H.; Carty, A. J.; Low, P. J. *Dalton Trans.* **2003**, 1099.

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Positively Charged Water Soluble Multi – Porphyrin Arrays for DNA Recognition

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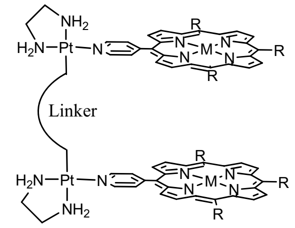
Cationic metal porphyrins are able to interact with DNA in various ways. Most commonly, these systems intercalate into DNA[1]. Zinc porphyrin $ZnTMPyP^{4+}$ was shown to interact with the Z form of poly d(GC)[2]. Z – DNA can be induced by divalent metal centers such as Cu(II) or Zn(II)[3] or dinuclear metal complexes[4] that interact with $(CG)_n$ units such as $d((CG)_3TTTT(CG)_3)$ or poly $d(GC)_n$. In order to observe a more selective coordination behaviour towards specific DNA conformations, we want to introduce a recognition unit consisting of metal porphyrins and a linker in between those porphyrins. Different linkers and variations of R will allow to define the parameters that influence the binding behaviour towards various DNA double helices conformations.



[1] S. Mohammadi, N. Gresh, K. Hillairet, E. Taillandier, *Biochemistry* **1998**, *37*, 6165 .
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[3] B. Spingler, C. Da Pieve, *Dalton Trans.* **2005**, 1637.
[4] B. Spingler, P. M. Antoni, *Chem. Eur. J.* **2007**, *13*, 6617.

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Cu-BTC Based Metal-Organic Frameworks as Catalysts for the Oxidation of Cyclohexene

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Hönggerberg, HCI, CH-8093 Zurich

Due to their beneficial properties, metal-organic frameworks (MOFs) are considered to act as potential heterogeneous catalysts.

Cu-BTC is a material built from Cu(II) dimeric units that are coordinated by benzene-1,3,5-tricarboxylate linkers. This results in a paddle-wheel structure where each Cu^{2+} ion exhibits one coordination site which is occupied by a weakly bound water molecule that can be exchanged by a substrate molecule during catalytic reactions. [1]

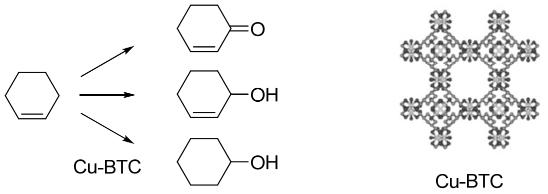

Figure 1: Oxidation of cyclohexene catalyzed by Cu-BTC

A targeted modification of the framework structure (e.g. by using the mixed-linker concept [2]) offers the possibility to tune the nature and accessibility of the active sites and to influence the catalytic properties. The potential of these Cu-BTC based materials for catalytic applications is demonstrated using the oxidation of cyclohexene as a test reaction.

[1] K. Schlichte, T. Kratzke, S. Kaskel, *Microporous Mesoporous Mater.* **2004**, *73*, 81.
[2] W. Kleist, F. Jutz, M. Maciejewski, A. Baiker, submitted for publication.

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New complexation strategy and relaxation properties of the conformation-switching complex $\{Mes[Gd(DO3A)(H_2O)_2]_3\}$

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[2]UMR cnrs 6521, Université de Bretagne Occidentale, 6 avenue Victor Le Gorgeu – CS 93837, 29238 Brest Cedex 3, France

The gadolinium complex $\{Mes[Gd(DO3A)(H_2O)_2]_3\}$ (figure 1) was designed as a MRI contrast agent, in line with a project dealing with small molecules containing several Gd(III) complexes around a central core.

According to relaxation measurements and ICP-MS, the standard complexation method, with $GdCl_3$ at pH 5.8, leads to an undesired compound with only two Gd(III) ions and only one water molecule in the inner sphere of the formed complexes. A new complexation strategy, involving precomplexation with Mg^{2+} at higher pH followed by a transmetallation, tracked by relaxation, has been developed to get the desired Tris-Gd complex.

This work presents the complexation methods, the relaxivity properties of the complexes and the evidences of the formation of the two different compounds. Moreover, we suggest a possible mechanism for the conformation change of the Bis-Gd complex, via amine protonation and acetate capping.

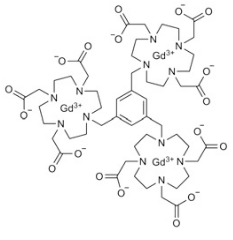

Figure 1 : *$\{Mes[Gd(DO3A)(H_2O)_2]_3\}$*

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High and low valent Rhenium complexes containing a very small substitution labile N-heterocyclic ligand

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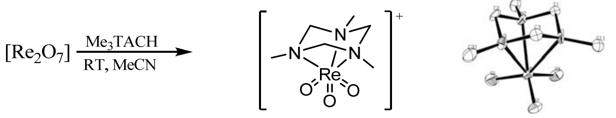
Stable Rhenium complexes with the *fac*-$\{ReO_3\}^+$-core containing a substitution labile ligand have a high potential as precursor complexes and could widen the range of known Rhenium complexes containing this metal core. Often serving as a model system for its lighter homologue, Tc, similar reactivites may apply. A variety of complexes containing the *fac*-$\{TcO_3\}^+$-core[1, 2] are being investigated as possible candidates for new labeling strategies, such as the [2+3]-cycloaddition approach.[3] Ligand displacement could allow access to new routes of synthesizing complexes with possible radiopharmaceutical applications.



To our knowledge, no rhenium complexes containing the smallest ligand of the triazacycloalkane family, 1,3,5-trimethyl-1,3,5-triazacyclohexane (Me$_3$TACH) have been reported so far.

We report the synthesis and characterization of the two isolobal complexes $[Re(CO)_3(Me_3TACH)](OTf)$ and $[ReO_3(Me_3TACH)][ReO_4]$. The stability and reactivity of both complexes was studied. The lability of the small ligand renders both complexes to be metastable under ambient conditions, however it also allows for the weakly bound ligand to be substituted by stronger ligandes e.g. 1,3,4-triazacyclononane (TACN). This possibility allows access to a variety of metal complexes containing the *fac*-$\{Re(CO)_3\}^+$- and the *fac*-$\{ReO_3\}^+$-core via ligand displacement reactions.

[1] H. Braband, U. Abram, *Inorg. Chem.* **2006**, *45*, 6589-6591.
[2] Y. Tooyama, H. Braband, B. Spingler, U. Abram, R. Alberto, *Inorg. Chem.* **2008**, *47*, 257-264.
[3] H. Braband, Y. Tooyama, T. Fox, R. Alberto, *Chem. Eur. J.* **2009**, *15*, 633-638.

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Synthesis and Characterization of Chromium Complexes

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There is great interest in developing complexes with two trans σ-alkynyl ligands[1] due to their potencial application as building blocks for use in the construction of dinuclear or oligonuclear nanoscale electronic devices. Complexes such as $[L_nM\text{-}C{\equiv}C\text{-}C{\equiv}C\text{-}ML_n]$ are expected to display non-linear optical propierties or may have applications as molecular devices [2]. Much of this interest has been prompted by their rich redox chemistry, their unique electronic features, and the obvious connection to molecular wires having the ability to shuttle electrons across nanometer distances [3].

We are interested in synthesizing unsymmetric chromium(II)bis-acetylide complexes and dinuclear complexes of the type $[L_nM\text{-}C{\equiv}C\text{-}C{\equiv}C\text{-}ML_n]$ (M = Cr; L = $(CH_3)_2PCH_2$ $CH_2(CH_3)_2$ with bis(dimethylphosphino)ethane as ligand, which is an excellent chelating ligand to stabilize carbon rich species in a simple and a facile way.

[1] S. Kheradmandan, K. Heinze, H. W. Schmalle, H. Berke, *Angew. Chem. Int. Ed. Engl.* **1999**, 38, 2270-2273.
[2] C. B. Gorman, R. L. Carrol, *Angew. Chem.* **2002**, *114(23)*, 4556-4579, *Angew. Chem. Int. Ed. Engl.* **2002**, *41(23)*, 4378-4400
[3] N. Robertson, C. A. McGowan, *Chem. Soc. Rev.* **2003**, *32(2)*, 96-103

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High efficient donor–acceptor ruthenium complex for dye-sensitized solar cell applications

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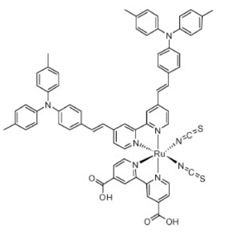
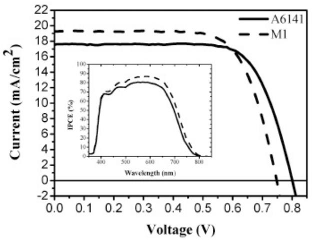
A highly efficient heteroleptic ruthenium (II) complex cis-di(thiocyanato)(4,4'-dicarboxylicacid-2,2'-bipyridine)(4,4'-di-(2-(4-ditolylaminephenyl)ethenyl)-2,2'-bipyridine) ruthenium (II) (IJ-1) was synthesized and characterized, which when anchored on nanocrystalline TiO2 films exhibited high power conversion efficiency, 10.3%,[1] and incident photon to electron conversion efficiency, 87%.





[1] J. Yum, I. Jung, C. Baik, J. Ko, M. K. Nazeeruddina, M. Grätzel. *Energy Environ. Sci.,* **2009**, *2*, 100.

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Sublimation not and Innocent Technique for Iridium Emitters

Etienne Baranoff, Philippe Bugnon, Claudia Barolo, Libero Zuppirolli, Michael Graetzel, and Md. K. Nazeeruddin

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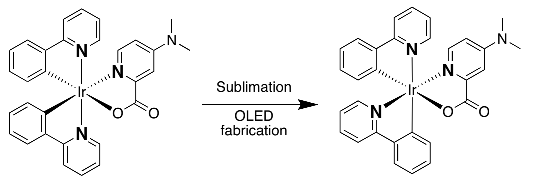
School of Basic Sciences, EPFL, CH-1015 Lausanne, Switzerland

Sublimation and vacuum deposition are techniques commonly used for purification of compounds and thin-films preparation in Organic Light-Emitting Devices (OLEDs). Vacuum-processed devices exhibit usually higher efficiencies than simpler polymer-based devices.

However, recently we observed the isomerization of the green dopant **N984** during sublimation.[1]



pure *meridional*-isomer **N984** mixture containing *facial*-isomer **N984b**

Solution-[2] and vacuum-processed OLEDs are compared to show the impact of the isomer on the devices performances.

[1] E. Baranoff, S. Suàrez, P. Bugnon, C. Barolo, R. Buscaino, R. Scopelliti, L. Zuppiroli, M. Graetzel, Md. K. Nazeeruddin, *Inorg. Chem.* **2008**, *47*, 6575.
[2] H. J. Bolink, E. Coronado, S. G. Santamaria, M. Sessolo, N. Evans, C. Klein, E. Baranoff, K. Kalyanasundaram, M. Graetzel, Md. K. Nazeeruddin, *Chem. Commun.* **2007**, 3276.

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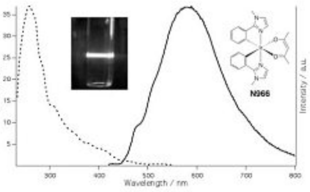
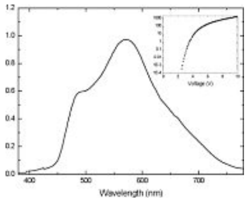
Panchromatic Phosphorescence Emission from a Single Molecule

Etienne Baranoff, Henk J. Bolink, Filippo De Angelis,
K. Kalyanasundaram, Michael Grätzel, and Md. K. Nazeeruddin

Laboratory for Photonics and Interfaces, Laboratoire d'Optoélectronique des Matériaux,
School of Basic Sciences, EPFL, CH-1015 Lausanne, Switzerland

To date organic white light-emitting devices (WOLEDs) are obtained by combining multiple emission which requires complex device architectures, which has so far greatly hindered their market entry. Therefore, the development of a white light-emitting phosphorescent single transition metal complex is very much desired.





We obtained an iridium complex exhibiting very borad photo- and electroluminescence. Theoretical calculations rationalize the reasons behind such broad emission, opening the way for generalization of this new strategy for WOLEDs development. Our result demonstrates that low cost white light-emitting OLEDs with a single emitting component can be achieved.

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Flame-made Pt/K/Al_2O_3 NO_x storage-reduction catalysts

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NO_x storage-reduction (NSR) catalyst can trap exhaust NO_x under fuel lean conditions on an alkali- or alkaline earth metal in the form of metal-nitrates. Here Pt/K/Al_2O_3 was prepared using flame spray pyrolysis (FSP)[1]. Raman investigations showed amorphous K_2CO_3 to be the active storage compound. The K-based NSR material showed better NO_x storage performance than the classical Ba based system, during the lean period and the switch from fuel lean to fuel rich conditions (Figure 1). This superior performance was attributed to good K distribution in the sample as evidenced by STEM combined with EDX analysis.

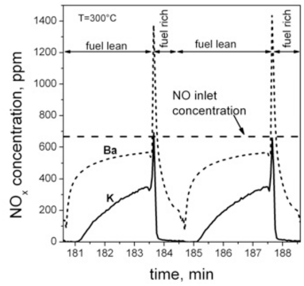

Figure 1: Comparison of K/Pt/Al_2O_3 and Ba/Pt/Al_2O_3 during NSR testing.

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Novel thiocyanate free cyclometalleted ruthenium sensitizers upon anchoring to nanocrystalline TiO_2 films exhibit remarkable incident monochromatic photon-to-current conversion efficiency 83%, and the solar cell employing a liquid based electrolyte exhibited a short circuit photocurrent density of 17.10 mA/cm^2, the open circuit voltage was 802 mV and a fill factor of 0.74, corresponding to an overall conversion efficiency of 10.08% at standard AM 1.5 sunlight.[1] To understand the structural, electronic and optical properties of the cyclometalleted ruthenium sensitizers we have investigated using both density functional theory (DFT) and time dependent DFT (TDDFT). Our results show that the HOMO is located mostly on ruthenium and cyclometallated ligand where as the LUMO is on 4,-carboxylic acid-4'-carboxylate-2,2'-bipyridine. Molecular orbitals analysis confirmed the experimental assignment of redox potentials, and TDDFT calculations allowed assignment of the visible absorption bands. The present findings provide new design criteria for the next generation of ruthenium sensitizers, which foster widespread interest in engineering of new sensitizers that allow an interaction with the I^-/I_3^- redox couple.

[1] T. Bessho, E. Yoneda, J.-H. Yum, M. Guglielmi, I. Tavernelli, H. Imai, U. Rothlisberger, M. K. Nazeeruddin and M. Grätzel, *J. Am. Chem. Soc.*, **2009**, *131*, 5930.

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Cu(II) Complexes with 5'-GMP and poly d(GC): Structure Determination with the Help of Pulsed EPR Spectroscopy

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Z-DNA is a higher energetic form of DNA. In contrast to the normally prevailing right-handed form of DNA (B-DNA), Z-DNA presents a left-handed helix.[1] Substochiometric amounts of dicopper and dinickel complexes were able to convert poly d(CG) from the right- to the left-handed conformation.[2]

In this work, we have used Cu(II)-GMP (GMP: 5'-guanosine monophosphate) as an entry system to understand the interactions between copper and polynucleotides with the help of EPR. The first aim of the present work was to carry out a detailed analysis of the electronic and geometric structure of the CuGMP complex.[3] In addition, we have studied the interaction of copper with poly d(GC). Here, always two copper species were found. Despite the additional challenge in form of extensive signal overlap, it was possible to describe the coordination environment of the two copper species, both bound to poly d(GC). Continuous-wave and pulse EPR methods like ENDOR and HYSCORE provided unique information about the structure of these copper centers through an elaborate mapping of the hyperfine interactions between the unpaired electron of the Cu(II) ion and the magnetic nuclei of the nucleotide ligand.

[1] B. Spingler, F. Zobi, P. M. Antoni, A. Medina-Molner, R. Alberto, *Chimia* **2005**, *59*, 826. B. Spingler, C. Da Pieve, A. Medina-Molner, P. M. Antoni, M. G. Santangelo, *Chimia* **2009**, *63*, 153
[2] B. Spingler, P. M. Antoni, *Chem. Eur. J.* **2007**, *13*, 6617.
[3] M. G. Santangelo, A. Medina-Molner, A. Schweiger, G. Mitrikas, B. Spingler, *J. Biol. Inorg. Chem.* **2007**, *12*, 767

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Kinetic Resolution of Chiral Phosphodiesters by Artificial Metalloenzymes Based on Biotin-Streptavidin Technology

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In contrast to organometallic catalysts, enzymes are particularily efficient at hydrolyzing inert phosphodiester and amide linkages. In a biomimetic spirit, incorporation of a biotinylated dinuclear metal complex in streptavidin affords artificial hydrolases for the kinetic resolution of racemic phosphodiesters. A chemogenetic optimization scheme allows to optimize both the activity and the selectivity of the artificial metallonuclease. Combining, kinetic data, mutagenesis and screening of various substrates allows us to present a hypothesis on the key enantiodiscriminating interactions which afford exquise *E* selectivity factors. In addition, our recent efforts on ds-DNA hydrolysis with these artificial nucleases will be presented.

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Novel 3D conductive backbones for enhanced efficiency in photovoltaics and photolysis

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We shall introduce innovative strategy that simultaneously amplifies the harvesting of photons and improves charge collection in a new kind of nanostructure composite electrode for dye sensitized solar cells and photolysis for hydrogen production. As noted by Gratzel et al. in 2006 [1], charge percolation back to the transparent conductive (TCO) electrodes takes milliseconds. This slow charge extraction increases chances of electron-hole recombination at the mesoporous TiO_2 - electrolyte interface. This limitation has proven long lasting over the last 15 years and limited efficient DSCs to be used with only a handful of electrolytes that offer low recombination rates. Herein, we propose to use a innovative three-dimensional charge collecting network to improve the efficiency of charge transport in photovoltaics and photolysis in general, DSCs and hematite water splitting in particlular. Therefore, the essence of the idea is predicated upon a composite cathode in which current collector, photoactive element, sensitizer and electrolyte are integrated into a single unit without sacrificing light harvesting capabilities.

[1] Wang et al. Characteristics of high efficiency dye-sensitized solar cells. J Phys Chem B (2006) vol. 110 (50) pp. 25210-25221.

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The Self-Assembly of Lanthanides with Dissymmetric Tripodal Ligands

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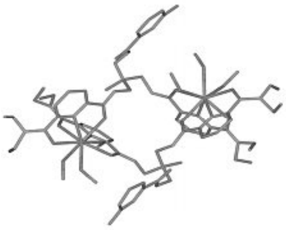
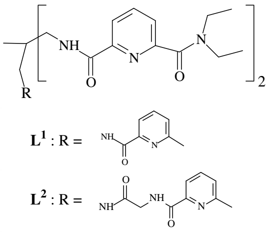
The improvement of the Ln(III) luminescent and magnetic properties requires a judicious design of ligands, in particular tripods[1]. In this work, two new asymmetric tripodal ligands $\mathbf{L}^1$ and $\mathbf{L}^2$ differing by the length of the bidentate pendant arm (see below) have been synthesized, and their self-assembly with Ln(III) was investigated. The complexes were characterized in acetonitrile solution by means of spectrophotometry, ES-MS and luminescence. These ligands are supposed to provide a coordination cavity for eight-coordinated lanthanide cations, and to form monometallic complexes. However, the X-ray crystal structure of the europium complex with $\mathbf{L}^1$ ([M]/[**L**] = 1:1) revealed a dimeric form in the solid state. Herein, the solution properties of Ln(III) complexes with both ligands and the effects of the spacer length will be discussed.





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