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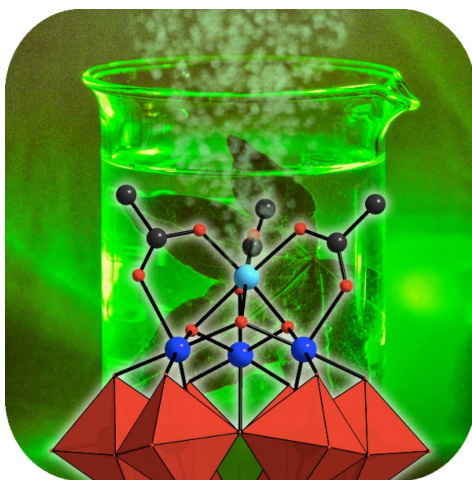
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Natural Born Catalysts: Photocatalytic Water Oxidation by Molecular Metal OxidesM. Bonchio¹¹University of Padova and ITM-CNR UoS-PD, Department of Chemical Sciences, via Marzolo 1, 35131 Padova, Italy

The oxygen-evolving complex of photosystem II (PSII-OEC) in green plants, algae and cyanobacteria, is the unique catalytic site where, upon illumination, H₂O bonds are oxidized to form O₂. The natural OEC is a tetramanganese-calcium-oxo cluster (Mn₄O₅Ca), harbored within the PSII complex, with a flexible and adaptive coordination environment provided by the protein residues. In particular, carboxylate ligands play a major role in the assembly of the OEC cluster, bridging Mn ions and the Ca²⁺ hetero-site. In order to mimic the PSII-OEC structure and activity, special attention has been dedicated to tetra-nuclear metal catalysts, including also Mn-based complexes. However, only few ruthenium or cobalt tetra-metallic cores have been recognized as competent oxygen evolving catalysts under photocatalytic conditions. We focus herein on a unique tetra-manganese core stabilized by a hybrid set of ligands, including an all-inorganic tungstosilicate platform and three acetate bridges. The resulting polyanion, [Mn^{III}₃Mn^{IV}O₃(CH₃COO)₃(A-α-SiW₉O₃₄)]⁶⁻ (**Mn₄POM**), displays striking similarities with the natural OEC in its S₀ state, *vis-à-vis* the Mn₄-oxo structure and its Mn^{III}/Mn^{IV} mixed-valency. Our results confirm that **Mn₄POM** undergoes fast and multiple electron transfers under visible light irradiation, leading to water photo-oxidation and oxygen evolution. The structural analogy with the natural photosynthetic catalyst is thus nicely complemented by a unique functional behavior, which follows a bio-inspired mechanism.[1-5]



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High Oxidation State N-Heterocyclic Carbene Molybdenum Alkylidene Complexes: Functional Group-Tolerant Olefin Metathesis Catalysts

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What is still a challenging task in olefin metathesis is a single site catalyst, which is highly active, both in terms of turn-over number (TON) and turn-over frequency (TOF), which is tolerant to water, air and number of functional groups with high stereo- and region-selectivity. In search for olefin-active metathesis catalysts based on a cheap metals and fulfill all the above mentioned criteria, the first N-heterocyclic carbene (NHC) complexes of *Schrock* molybdenum imido alkylidene bis(triflate) complexes have been synthesized. Unlike existing bis(triflate) complexes, the novel 5-fold coordinated 16-electron Mo-complexes contain two carbenes, *i.e.* a *Schrock* carbene and an NHC. Single crystal X-ray analysis revealed that the above mentioned complexes are distorted square pyramidal (SP) with one triflate (OTf) ligand *trans* to the NHC. In course of a metathesis reaction, this triflate leaves the complex and generates a trigonal bipyramidal cationic 14-electron Mo-NHC complex (¹⁹F-NMR studies). The most important observation of this type of catalysts is active in ring-closing metathesis (RCM), cross-metathesis (CM), the cyclopolymerisation of α,ω -diynes and ring-opening metathesis polymerisation (ROMP). Monomers containing functional groups, *e.g.*, *sec*-amine, hydroxy, and carboxylic acid moieties, which are not tolerated by the existing variations of *Schrock* catalysts, can be used. This novel class of catalysts displays substantial activity even at high temperatures (140 °C), *e.g.*, in RCM. Based on the observation that bistriflate complexes show a coalescence temperature for the two triflate groups, an activation mechanism based on a Berry-type pseudorotation, *i.e.* interconversion between trigonal bipyramidal (TBP) configurations through a square planar (SP), is proposed. Activation of the catalysts through the release of one triflate in the SP configuration is in full accordance with the observed reactivity of both neutral and cationic Mo-imido alkylidene NHC complexes and with ¹⁹F-NMR. Furthermore, reactions of the bis(triflate) NHC complexes with one equivalent of a fluorinated alkoxide (*e.g.*, -OCH(CF₃)₂, -OC₆F₅, -OCCH₃(CF₃)₂) or with Ag⁺B[3,5-(CF₃)₂C₆H₃]₄⁻ in dichloroethane afforded the corresponding monoalkoxide and the cationic imido alkylidene-NHC complexes. This particular feature is the presence of the NHC ligand, which delocalizes the cationic charge and stabilizes the molybdenum center. The structures of all compounds have been determined by single crystal X-ray diffraction and their reactivities in various olefin metathesis reactions have been explored. In selected metathesis reactions, TONs up to 545,000 have been reached. Nonetheless, Mo-imido alkylidene NHC complexes with one electron-withdrawing fluorinated alkoxide and the corresponding cationic complexes in which the remaining triflate replaced by B[3,5-(CF₃)₂C₆H₃]₄⁻ afforded remarkably active and functional-group tolerant metathesis catalysts. Employing different NHCs such as triazole-2-ylidene, benzimidazolylidene and CAAC (Cyclic Alkyl Amino Carbene) provides access to another novel class of Mo-NHC alkylidene complexes. It turned out that the Mo-imido alkylidene NHC complexes prepared very recently display a functional group tolerance that is unprecedented for high-oxidation state Mo-imido alkylidenes. These catalysts therefore hold great promise in both organic and polymer chemistry, where they allow for the use of protic monomers.

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Silver(I) N-heterocyclic complexes for C-C bond activation of alkyl nitriles and catalytic application in oxazoline synthesis

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N-heterocyclic carbenes (NHCs) have become increasingly prevalent ligands in the fields of organometallic chemistry and homogeneous catalysis [1]. A convenient route to form NHC transition metal complexes is the *in situ* generation of an Ag-NHC complex from reaction of azolium salts with Ag₂O, followed by transmetalation with a different metal [2]. However, to date little attention has been paid to the Ag-NHC intermediates regarding complex formation and potential catalytic applications [3].

We show that generation of Ag-NHC complexes from azolium salts in refluxing CH₃CN results in a selective C-C bond cleavage and the formation of [(NHC)Ag(CN)] complexes. This bond activation can also be extended to other alkyl nitrile reagents [4].

Furthermore, we will demonstrate the catalytic properties of a series of Ag-NHC complexes in oxazoline formation *via* aldol condensation. These highly active systems disclose new possibilities for applications of easily accessible silver carbene complexes.



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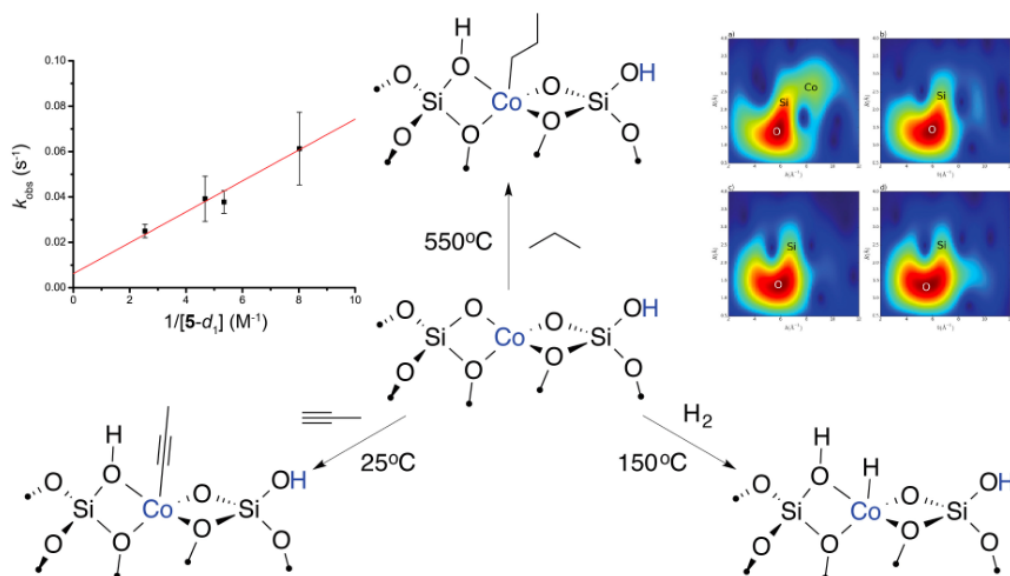
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C-H Activations Catalyzed by Transition-Metal Ions Isolated on Metal Oxide Surfaces

D. P. Estes¹, G. Siddiqui¹, F. Allouche¹, K. V. Kovtunov², O. V. Safonova³, A. Trigub⁴, I. V. Koptuyug², C. Copéret¹

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Transition metal ions supported on metal oxides have been shown to catalyze the conversion of hydrocarbons (e.g. dehydrogenation of alkanes, alkane homologations). These reactions have to involve a C-H bond activation step. However, the mechanism of these transformations is still not well understood. Combining surface organometallic chemistry and thermolytic molecular precursor approaches, we have prepared isolated metal ions on silica surfaces (e.g. Fe, Co), which display good activity in the dehydrogenation of propane. Using these molecularly defined surface sites, we have performed detailed mechanistic investigations of this reaction as well as related reactions (propene hydrogenation (the reverse process) and alkyne trimerization). All data (kinetic measurements, isotopic labeling studies, kinetic isotope effects, and comparison with molecular analogues) are consistent with a C-H bond activation mechanism involving 1,2 addition across a M-O bond.



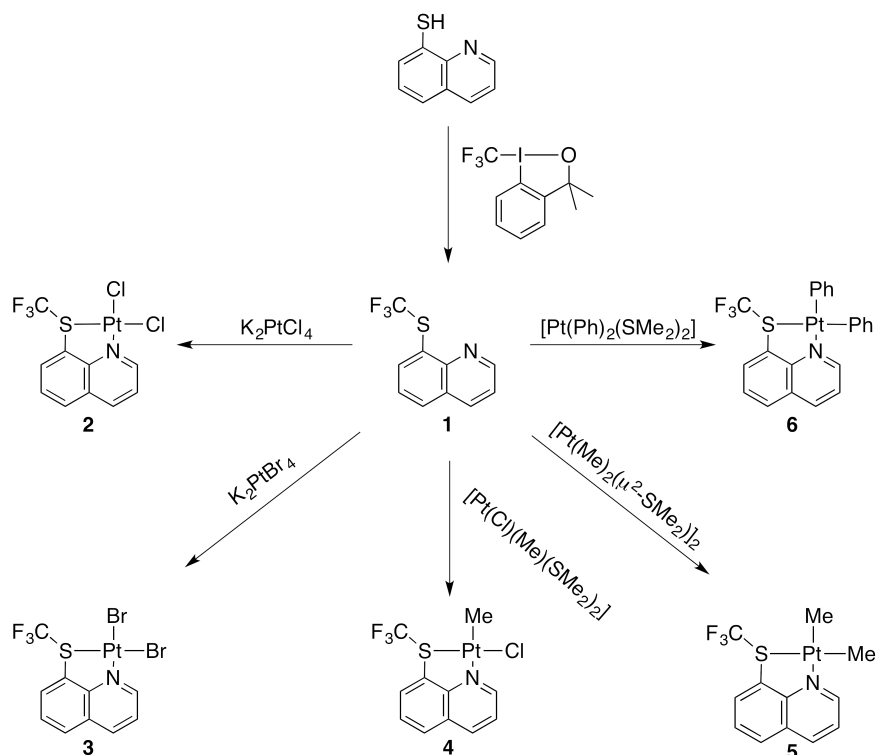
Exploring Trifluoromethylthioethers as ligands - Platinum(II) complexes of 8-(trifluoromethylthio)quinoline

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To date, metal complexes with trifluoromethylthioether ligands (RSCF₃) are not well studied, due to the limited availability of synthetic methods in the past and the prominence of group 15 ligands.^[1-3] Alkyl-, aryl- and perfluoroarylthioether ligands however are well known and have catalytic applications.^[4-5]

To explore the properties of RSCF₃ ligands the N,S-bidentate ligand 8-(trifluoromethylthio)quinoline (**1**) was synthesized by electrophilic trifluoromethylation of 8-thioquinoline. Ligand **1** was reacted with platinum(II) precursors K₂PtCl₄, K₂PtBr₄, cis-[Pt(Cl)(Me)(SMe₂)₂], [Pt(Me)₂(μ²-SMe₂)₂] and cis-[Pt(Ph)₂(SMe₂)₂] to form the corresponding complexes.



Complexes **2-6** were obtained in high yield, are air- and moisture-stable and soluble in most organic solvents with exception of strongly coordinating solvents such as MeCN and DMSO, which decoordinate the ligand.

Complexes **2-6** were characterized by elemental analysis, X-ray and ¹H, ¹³C, ¹⁹F, ¹⁹⁵Pt NMR spectroscopy and compared to their alkyl (RSCH₃) analogues and their reactivity investigated.

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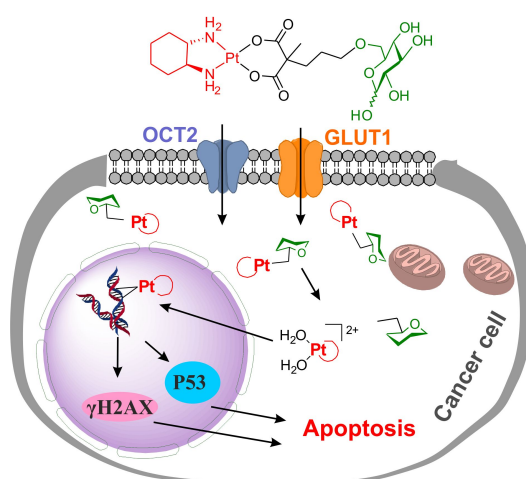
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D-Glucose-Platinum(II) Conjugates for Targeted Delivery of Platinum to Cancer CellsM. Patra, S. J. Lippard^{1*}¹Massachusetts Institute of Technology

The three FDA approved platinum anticancer drugs, cisplatin, carboplatin and oxaliplatin, are widely used in the clinic to treat various forms cancer including testicular, ovarian, cervical, head and neck, non-small-cell lung, and colorectal cancer.¹ Despite their phenomenal clinical success, however, the undesired side effects such as nephrotoxicity, myelosuppression, peripheral neuropathy, ototoxicity, and nausea^{1b,2} are main drawbacks of platinum-based chemotherapy.^{1b,2} The side effects can in principle be mitigated by introducing tumor-targeting properties into platinum anticancer compounds, thereby reducing nonspecific platinum accumulation in healthy tissues. Glucose transporter GLUT1 is overexpressed in many human cancers and its expression levels in tumor biopsy samples correlate well with poor prognosis.³ Attachment of D-glucose to platinum anticancer compounds to target delivery to cancer cells has therefore been an attractive strategy for selective killing of the tumor over healthy tissue.⁴ The design, synthesis, in vitro anticancer activity, in-depth characterization of the cellular uptake mechanism and the subcellular target of D-glucose-platinum(II) conjugates will be presented in this research seminar.⁵ This work was supported by a grant from the US National Cancer Institute.



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Red-light activated photoCORMs of Mn(I) species bearing symmetric substituted 2,2'-azopyridines.

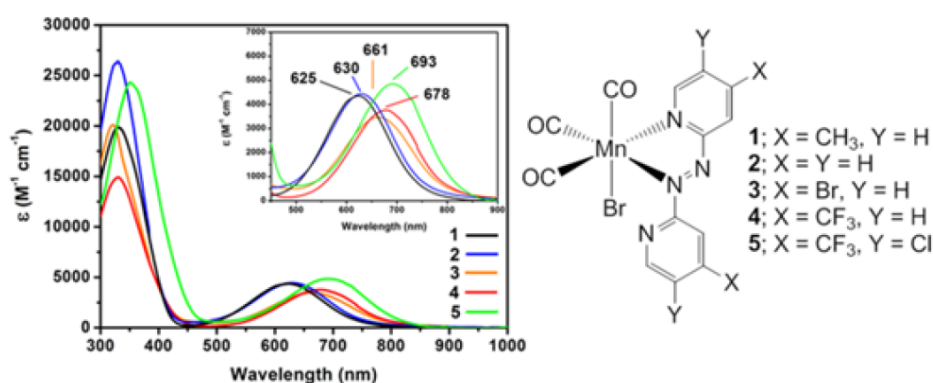
E. Kottelat¹, A. Ruggi¹, F. Zobi^{1*}

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Carbon monoxide (CO) has been acknowledged as a fundamental neurotransmitter in humans and there is a growing interest in its pharmacological or medical applications. As nitric oxide and hydrogen sulfide, CO is endogenously produced in animals. These neurotransmitters are involved in several cellular, physiological and pathological pathways, such as vasodilatation, endothelial injuries, inflammation. Organometallic carbonyl complexes are best suited to play the role of CO carriers. Targeting of the molecules to local injuries can thus be achieved by modifying the coordination sphere of the metal ion via a proper selection of ligands or by appending CO releasing molecules (CORMs) to biomolecules. Manganese-based CORMs, for example, are activated by exposure to UV-light and are known as photoCORMs^[1].

One of the great challenges in the design of photoCORMs lies in their sensitivity to visible light. Most of known photoCORMs have suffered from this fundamental drawback with few exceptions. In particular the group of Mascharak^[2] has endeavored to develop rational strategies to visible light-activated CORMs and has introduced a series of carbonyl Mn(I) complexes with conjugated ligands of the 2-pyridyl-N-(2-methylthiophenyl) methylenimine and 2-phenylazopyridine type which show MLCT bands with maxima at ca. 585 nm. These molecules represent probably the most significant improvement the field has seen in the recent years.

In this work, we report the synthesis, characterization and photochemical behaviour of the above mentioned complexes. The systematic substitution of the 2,2'-azopyridine with weak donating to strong deactivating substituents (EWG) lead to the progressive bathochromic shift of the MLCT absorption band maximum from 625 nm to 693 nm (Fig. 1). Exposure of solutions of complexes 1-5 to low-power visible light (≥ 625 nm, red light) resulted in CO photorelease as evidenced by the myoglobin assay. Furthermore, the MLCT band of complexes with strong EWG tails beyond the visible region of the spectrum in the near infrared and in one case photodecomposition could also be promoted at 810 nm.



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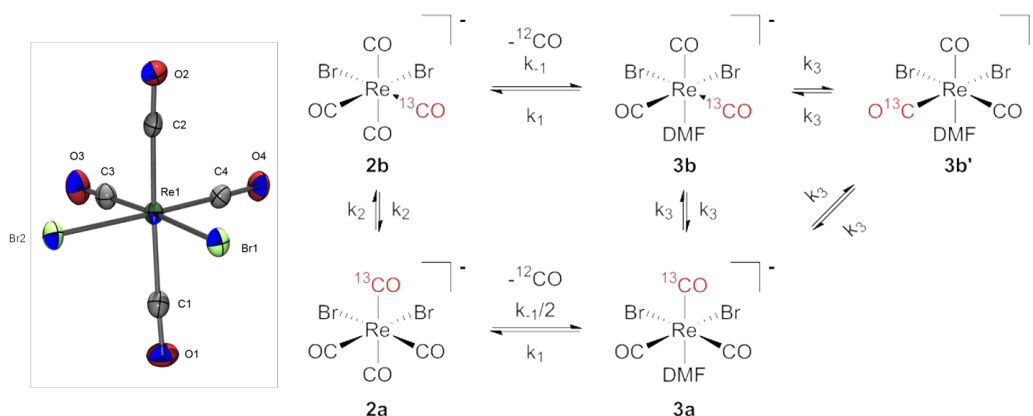
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Not so similar after all. Fundamental differences in reactivity of $fac-[M(solvent)_3(CO)_3]^+$ ($M = Re, {}^{99}Tc$) with CO

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In the context of theranostics, the $fac-[M(CO)_3]^+$ ($M = Re, Tc$) core has proven promising due to its high kinetic stability and the relative ease of ligand exchange on the three non-CO coordination sites.¹ The substitution kinetics of these three labile sites have been studied extensively in the past. On the other hand, the exchange of carbonyl ligands has only been investigated very sparingly, most prominently in the complex $fac-[{}^{99}Tc(CO)_3(H_2O)_3]^+$.² To the best of our knowledge, no comparable studies have been performed with rhenium. To determine the ideal reaction conditions for the synthesis of radiopharmaceuticals it is imperative to understand in-depth the behavior of both the rhenium and technetium starting materials. We have conducted a systematic study of the self-exchange kinetics of the carbonyl ligands in $[ReBr_3(CO)_3]^{2-}$ and its respective solvato complexes. We present a complete mechanism for the self-exchange of the CO ligands based on both experimental and computational considerations. The stable intermediate complex $[ReBr_2(CO)_4]^-$ was isolated and fully characterized. Surprisingly, for ${}^{99}Tc$ a fundamentally different behavior was observed under comparable conditions. A dissociative-interchange mechanism for its formation is proposed based on the kinetic data.



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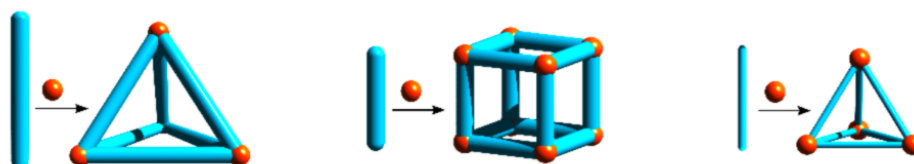
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Controlling architecture of coordination cages via the aspect ratio of the ligands

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It is possible to control the geometry and the composition of metallasupramolecular assemblies via the aspect ratio of their ligands. This point is demonstrated for a series of iron- and palladium-based coordination cages. Functionalized clathrochelate complexes with variable aspect ratios were used as rod-like metalloligands. A cubic $\text{Fe}^{\text{II}}_8\text{L}_{12}$ cage was obtained from a metalloligand with an intermediate aspect ratio. By increasing the length or by decreasing the width of the ligand, the self-assembly process resulted in the clean formation of tetrahedral $\text{Fe}^{\text{II}}_4\text{L}_6$ cages instead of cubic cages.



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Design Approaches to Blue and White Light Emitting Gold(III) Complexes

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During the past decennaries, transition metal complexes exhibiting interesting luminescent properties have been extensively investigated for applications in phosphorescent organic light emitting devices (PHOLEDs).¹ Organogold(III) complexes have been gaining increasing attention due to their promising emission properties.² The main problem being faced at the current time is the production of high-quality blue-emitting OLEDs. Three challenges emerge concerning the development of efficient blue triplet emitters. Poor chromaticity, low quantum efficiency and the short working lifetime. Recently, our group has demonstrated stable complexes based on monocyclometalated gold(III) framework displaying emission properties that rival the isoelectronic platinum(II) complexes.³ Utilizing a rational design approach, we have been able to render gold(III) complexes with blue and white light emission properties that has been previously unprecedented.⁴ These complexes have been investigated by detailed computational and photophysical studies and selected complexes by fabrication of devices. The tailored novel luminescent properties open-up further possibilities of applications of gold(III) complexes in light-emitting devices.

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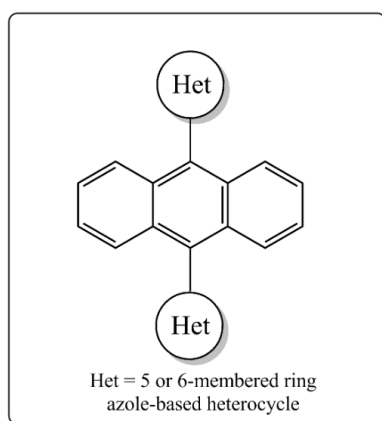
Anthracene-based ligands for new luminescent coordination polymersS. Vasylevskyi¹, K. Fromm^{1*}¹University of Fribourg

The design and synthesis of luminescent metal–organic complexes, polymers, and supramolecular frameworks are gaining interest as they find applications in molecular sensing, tunable emission for various light emitting devices (LEDs), and multiphoton upconversion devices [1, 2].

For numerous azole-based heterocyclic ligands it was shown that they can form a large panoply of building blocks which can be rigid or flexible [3]. As functional group, azole-based heterocycles have also potential in the design of new anthracene-based ligands. Anthracene derivatives with different azole-based heterocycles still have to be studied and explored.

The anthracene moiety is highly emissive in the UV-Vis region and involving this fragment into coordination polymers (CPs) can enhance the luminescent properties of the resulting materials [4]. Moreover, studying the crystal packing of the CPs with anthracene moieties will allow us to understand how different π - π stacking arrangements in the solid state influence the luminescent behavior of the compounds which are obtained. Furthermore, packing interactions between the anthracene fragment and the attached heterocycles will allow tuning the final luminescence properties. We will thus learn, using crystal engineering, which parameters bring significant influence on monomeric or dimeric emission inside of the solid CPs.

In this work we are going to present different bifunctional anthracene ligands which were designed for obtaining CPs with high potential for luminescent properties (Scheme 1). CPs of Cd(II) and Zn(II) will be presented. The studies of their luminescent properties are currently ongoing.



Scheme 1. Azole-based biheterocycle anthracene ligands.

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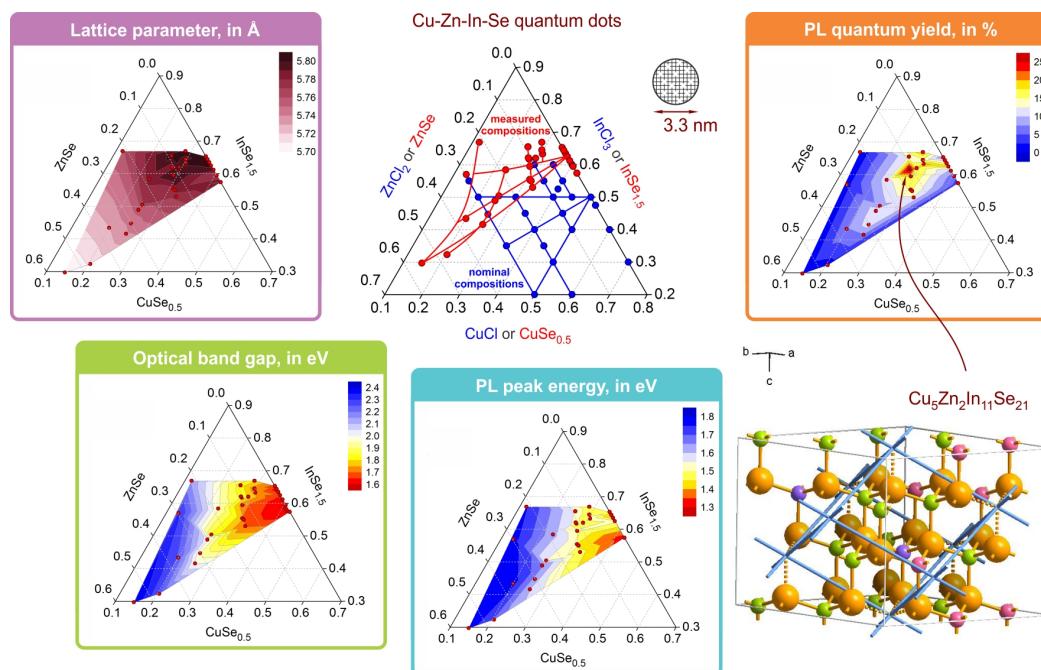
Beyond size effects: composition-tunable properties for quaternary Cu-Zn-In-Se quantum dots

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For multicomponent quantum dots (QDs), composition-dependent tuning of properties is superimposed on quantum confinement effects stemming for QD size. I-II-III-VI group semiconductor QDs represent excellent playground with broad miscibility ranges for binary chalcogenides and relatively large Bohr exciton radii, enabling size-dependent properties for QDs < 5 nm. In addition, certain compositions allow cationic defects to order within the lattice (*i.e.*, ordered defect compounds, ODCs).

Here we present our investigation of the composition-dependent properties of quaternary Cu-Zn-In-Se (CZISE) colloidal quantum dots. [1] We employ an amide-promoted synthesis, which can provide independent composition and size control for multicomponent chalcogenides. [2] Applying same reaction conditions, and varying the amount of introduced metal salts, we are able to vary the composition of CZISE QDs over a broad range while keeping QD size similar ($D_{\text{QD}} = 3.3$ nm, see Figure). This allows us to map several optical and structural properties as a function of CZISE QD composition, such as lattice constant, optical band gap, PL peak position, or PL quantum yield (see Figure). We find that the PL quantum yield peaks at a composition close to $\text{Cu}_5\text{Zn}_2\text{In}_{11}\text{Se}_{21}$. Experimental and theoretical work suggests that the high PL efficiency of this composition originates from the fact that it belongs to a family of ODC structures with parent ternary composition of $\text{Cu}_2\text{In}_4\text{Se}_7$ and $1/7$ concentration of atomic vacancies on cation site. These results can guide the development of high PL quantum yield materials.



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