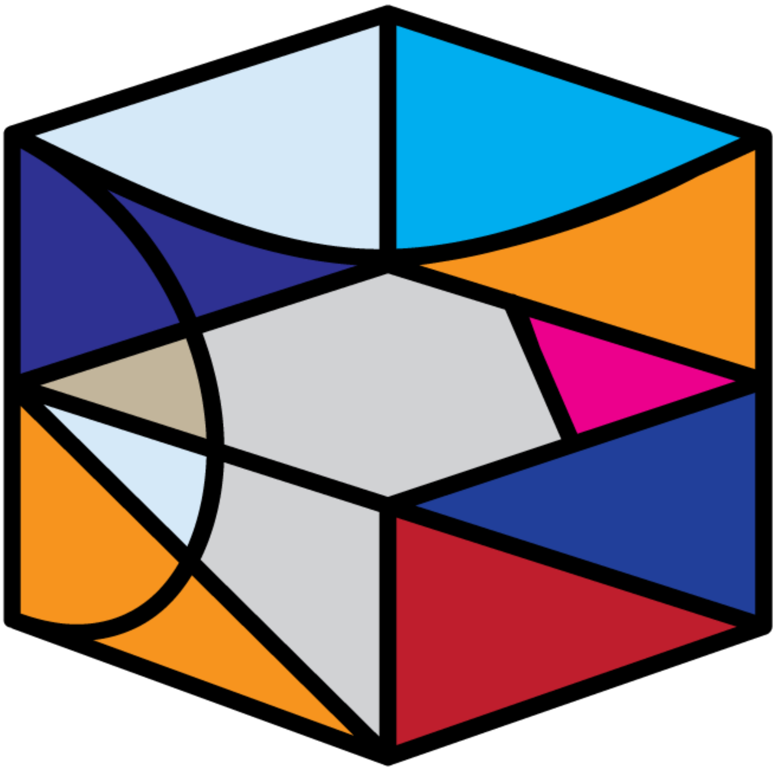

MADEMAT

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ORAL

POSTER

Tuesday 8/7/2025

8h30 -10h15	Registration & Coffee	
10h15-10h25	***Opening session***	Chairman : S. Cordier
10h25-11h15	**Invited talk: Stephanie Dehnen** Multimetallic Clusters: Atomically Precise Nanoobjects with Uncommon Properties	
11h15-11h40	**Thomas Fässler** Intermetalloid Clusters in Neat Solids and in Solution	
11h40-12h05	**Tatsuya Higaki** An Icosahedral [Fe$_{55}$] Paired with an Octahedral [Fe$_{6}$]	
12h05-12h30	**Stefano Zacchini** Molecular Alloy Carbonyl Nanoclusters	
12h30-14h	***Lunch & poster session***	
14h00-14h50	**Keynote Lecture: Jean-Yves Saillard** Electronic structure of atom precise Ag-rich and Cu-rich superatoms and supermolecules	Chairman : R. Gautier
14h50-15h15	**Franck Wagner** Bonding architecture of delocalized bonding in clusters and intermetallic compounds from DR analysis	
15h15-15h40	**Jianyu Wei** Theoretical Analysis of Bonding and Electronic Structure of Heteroatom Doped Coinage Metal Superatomic Nanoclusters	
15h40-16h05	**Helene Gerard** Modelling growth and dissolution of metallic copper cluster in the framework of nanoparticles chemistry	
16h05-16h45	***Coffee break & poster session***	
16h45-17h10	**Kaplan Kirakci** Polymer-Based Delivery Strategy for Mo$_{6}$ Clusters Radio/Photosensitizers	Chairwoman: M. Feliz
17h10-17h35	**Marian Amela-Cortes** Nanocomposite based on metal atom cluster for light-driven applications	
17h35-18h00	**Tomas Pribyl** Molybdenum Cluster Nanoparticles for Radiodynamic Cancer Cell Therapy	
18h00-18h25	**Eric Fuster-Navarro** Antibacterial Resins with Photoactive Octahedral Molybdenum Iodide Clusters	
18h25-21h30	***Poster session - Welcome drink and local specialties***	

Wednesday 9/7/2025

8h30-9h20	**Invited talk: Nanfeng Zeng** Surface Coordination Chemistry of Metal Nanomaterials	Chairman : X. Roy
9h20-9h45	**Kuan-Guan Liu** Rearrangement of Surface Coordination Structures of Silver Nanoclusters and Its Influence on the Luminescent Properties of Nanoclusters	
9h45-10h10	**Lisa Szczepura** Reactivity of terminal ligands coordinated to octahedral M$_6$ cluster cores	
10h10-10h35	**Rosa Llusar** Activation of H-H and H-Si Bonds Using Molybdenumn Sulfide Cluster Catalysts	
10h35-11h15	***Coffee Break & poster session***	
11h15-11h40	**Kamil Lang** Photocatalytic Potential of Octahedral Molybdenum Clusters: From Design to Application	Chairman : H.-J Meyer
11h40-12h05	**Kurt Kpoton** Clusters-polyoxometallates eco-compatible tandems for the production of hydrogen: from molecular assemblies to the device	
12h05-12h30	**Jun Zhou** Atomically precise palladium clusters and nanoparticles as catalysts for hydrogen production and hydrogenation reactions using organocobalt complexes	
12h30-14h	***Lunch & poster session***	
14h00-14h25	**Biswarup Pathak** Nanocluster Catalysis: Breaking Conventions Through Machine Learning and Artificial Intelligence	Chairwoman: M. Amela-Cortes
14h25-14h50	**Krishna Haldar** Unraveling the Role of Orbital Interaction in the Electrochemical HER of the Trimetallic AgAuCu Nanobowl Catalyst	
14h50-15h15	**Marta Feliz** Graphene Decorated with Mo$_3$S$_7$ Clusters for Gas Sensing	
15h15-15h40	**Jaroslav Zelenka** Enigmatic formation of hydrogen peroxide from molecular hydrogen by human metalloenzymes	
15h40-16h05	**Jhon Sebastian Hernandez Niño** Visible-Light-Driven Degradation of Phenolic Compounds by Mo$_6$I$_{12}$/g-C$_3$N$_4$ Systems	
16h05-16h45	***Coffee break & poster session***	
16h45-17h10	**Sen Tapasi** Probing the fluorescence intermittency of single metal nanoclusters	Chairwoman: L. Szczepura
17h10-17h35	**Yann Molard** Emissive hybrid organic-inorganic nanocomposites integrating octahedral M$_6$ nanoclusters	
17h35-18h00	**Rajarshi Sinha Roy** Generation of Orbital Magnetism by Light in Atomically Precise Metal Clusters	
18h00-18h25	**Adele Renaud** Octahedral Metal Cluster-based Building Blocks: Towards the Engineering of New Ambipolar Photoelectrodes for Solar Energy Conversion	

Thursday 10/7/2025

8h30-9h20	**Keynote Lecture: Xavier Roy** Next Level Superatomic Materials	Chairman : N. Zheng
9h20-9h45	**Takashi Yoshimura** Tuning Redox Potentials of Hexarhenium Complexes	
9h45-10h10	**Clement Falaise** A Journey into Super-Reduction of Wells-Dawson polyoxotungstate: Electron Storage in Metalâ€“Metal Bonds	
10h10-10h35	**Chen-Wei Liu** Reactivities of Copper Hydride Clusters with Terminal Alkynes: En Route to 2-Electron Superatom	
10h35-11h15	***Coffee Break & poster session***	
11h15-11h40	**Stephane Cordier** Exploring the Structure–Property Relationships in Transition Metal Clusters (Nb6, Ta6, Mo6) for Energy Applications	Chairman: T. Fässler
11h40-12h05	**Martin Köckerling** Nb_6/Ta_6 Metal Atom Cluster Materials: Facile Large Quantity Preparation and New Materials.	
12h05-12h30	**Hao Yuan** Record-high hyperpolarizabilities in atomically precise single metal-doped silver nanoclusters	
12h30-13h45	***Lunch & poster session***	
13h45-14h35	**Invited talk: Torsten Hegmann** The role of shape and solute-solvent compatibility on the efficacy of chirality transfer from nanomaterials to liquid crystals	Chairman: Y. Molard
14h35-15h00	**Jeanne Rebours** Sustainable circularly polarized emission from cluster-embedded bent-core liquid crystals systems for advanced optoelectronic applications	
15h00-15h25	**Hans-Christian Weissker** Optical Properties of Gold Clusters Following Surface-Modification by Hydrogen Exposure	
15h25-15h50	**Marianne Prévôt** Shaping Light: Bent-Core Liquid Crystals and Clustomesogens for High-Performance Circularly Polarized Devices	
15h50-18h00	Visit of Rennes / free time	
18h00-19h30	Reception at Rennes City Hall	
19h30-22h00	Colloquium banquet at "La Taverne"	

Friday 11/7/2025

8h40-9h20	**Special Keynote lecture: Roland Fischer** Living Libraries of Intermetallic Superatoms	Chairwoman: R. Llusar
9h20-9h45	**Jürgen Meyer** Niobium Oxyiodide Cluster Compounds from Heterogeneous Solid-State Reactions by means of Non-Conventional Reduction	
9h45-10h10	**Manfred Scheer** Polypnictogen ligand complexes as building blocks for supramolecular aggregations	
10h10-10h35	**Arnaud Tillet** Supramolecular self-assembly of nanotubes based on inorganic nano-ions and organic macrocycles	
10h35-11h15	***Coffee Break***	
11h15-11h40	**Yao Aimin** Exploring New Properties of Molybdenum Cluster Chalcogenides via First-Principles Calculations	Chairwoman: H. Gerard
11h40-12h05	**Regis Gautier** Thermoelectric Molybdenum Sulfides: A Theoretical Study	
12h05-12h15	***Concluding***	

ABSTRACT

Multimetallic Clusters: Atomically Precise Nanoobjects with Uncommon Properties

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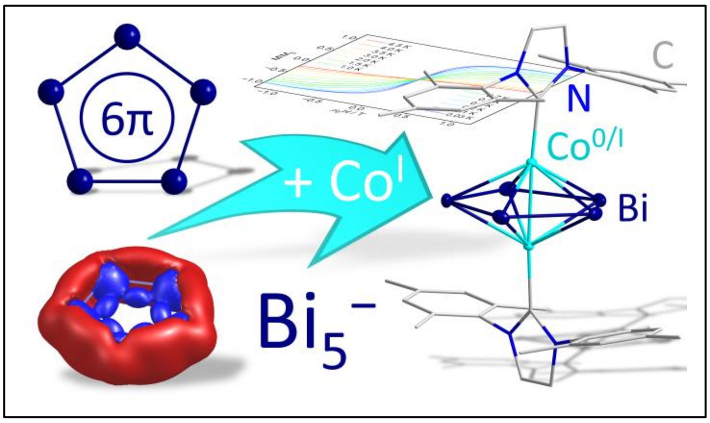
The synthetic access to cluster compounds and their numerous exciting properties have inspired many research groups worldwide to investigate them in the solid state, in solution, and in the gas phase.[1] In particular, clusters based on p-block elements in combination with d-/f-block metals have attracted a lot of attention,[2,3] with a recent focus on novel bismuth-based architectures.[4] Out of the many different synthetic approaches for corresponding clusters, we use Zintl anions in reactions with d- or f-block metal compounds to gain access to multinary clusters. Multimetallic clusters like $[K_2Zn_{20}Bi_{16}]^{6-}$,[5] $[Th@Bi_{12}]^{4-}$,[6] $[\{(cod)Ru\}_4Bi_{18}]^{4-}$,[7] or $[\{CpRu\}_3Bi_6]^{-}$,[8] $[Bi_6\{Zn(hmds)\}_2]^{2-}$,[9] or $[\{IMesCo\}_2Bi_5]$ (see figure) [10] demonstrate the broad range of unique structures and unprecedented bonding modes, including uncommon electronic as well magnetic features, and they also allow insight into cluster formation steps. In addition to these fundamental aspects, such species show potential for cluster-based bond activation, or as precursors for new intermetallics.



6π-Aromatic Bi_5^- and $[\{IMesCo\}_2Bi_5]$

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Intermetalloid Clusters in Neat Solids and in Solution

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Keywords: intermetalloid cluster, Zintl ion, Zintl phase, silicon clusters

For discrete heterometallic metal atom clusters that show a structural similarity to the solid-state structure of a related intermetallic, the term intermetalloid cluster was introduced [1] and numerous examples have been synthesized in solution.[2-3] As example reveal Cu-Sn intermetalloid clusters a nice series from soluble $[Cu@Sn_9]^{3-}$ to large $[Sn@Cu_{12}@Sn_{20}]^{12-}$ clusters [4] as well as linearly expanded Cu-Sn (bronze) rods in Na-Sn-Cu phases (Figure 1a and 1b). [5] Although silicon is by far the most important semiconductor material, a solution-based synthetic approach for unsaturated silicon-rich clusters is lacking. In this lecture, we also report a high yield synthesis with up to 30 g to soluble, polyhedral Si_9 clusters.[6] The separation of Si_9 from Si_4 clusters as they occur in $K_{12}Si_{17}$ is a new starting point for silicon-zintl chemistry. In addition to the isolation and structural characterization of a trisilylated $[MeHyp_3Si_9]$ cluster, metallated Si_9 clusters are also presented. On the basis of quantum chemical calculations, new silicon modifications based on Si_9 cluster building blocks seem reasonable.[7]

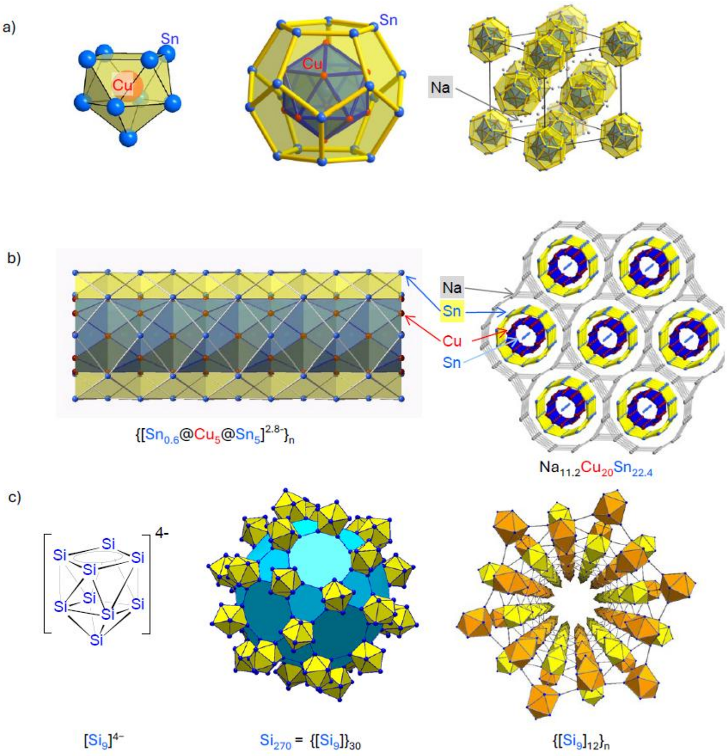

Figure 1. Examples of a) intermetalloid clusters in solution and in neat solids, b) nanorods of Cu and Sn atoms, and c) soluble Si_9 clusters and covalently linked aggregates

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An Icosahedral [Fe_{55}] Paired with an Octahedral [Fe_6]

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Recent progress in metal nanoclusters (NCs) has witnessed a large number of crystal structures and correlated properties that are unseen in bulk or nanoparticles of the metals. However, the reported examples of Fe NCs are still limited to subnanometer regime (*i.e.*, < 1 nm). Herein, we report atomically precise synthesis of hitherto the largest Fe nanocluster, $[Fe_{55}H_{46}(P\mathit{t}Bu_3)_{12}]^+$ ([Fe_{55}] in short hereafter) in the form of an ion pair with an anionic $[Fe_6H_8\{N(SiMe_3)_2\}_6]^-$ ([Fe_6]). Crystal structure of [Fe_{55}] shows a Mackay icosahedral Fe_{55} core protected by $P\mathit{t}Bu_3$ and hydrides. The chemical formula of [Fe_{55}][Fe_6] was confirmed by electrospray ionization mass spectrometry. X-ray absorption fine structure revealed the oxidation state of Fe atoms in [Fe_{55}][Fe_6] as well as the coordination number and bond distances, which are consistent with the crystallographic and mass spectrometric analyses. This work provides atomic insight into the stable size and structure of low-valent Fe NCs.

I. INTRODUCTION

Atomically precise synthesis of metal nanoclusters (NCs) has enabled the exploration of novel structures and functionalities unseen in bulk or conventional nanoparticles. The dramatic progress in the field is driven by structure determination by X-ray crystallography because structural elucidation at the nanoscale is typically elusive when using conventional techniques, especially for the interface between the metal core and the surface ligands. Significant effort has been made to obtain valuable information on the structural evolution with the increase in size, which enables to construct a library of crystal structures in order to map out the size/structure dependent properties. Recent advancement in correlative studies has witnessed the renaissance of coinage-metal (i.e., gold, silver, and copper) NCs protected by a wide range of surface-protecting ligands. In contrast, a family of ligand-protected iron clusters is still limited to smaller size regions below 1 nm in diameter.

II. RESULTS & DISCUSSION

Herein, we report hitherto the largest crystallographic structure of 55-iron-atom NCs, $[Fe_{55}H_{46}(P\mathit{t}Bu_3)_{12}]^+$, paired with an anionic $[Fe_6H_8\{N(SiMe_3)_2\}_6]^-$ ([Fe_{55}] and [Fe_6] for short, respectively) [1]. The [Fe_{55}] exhibits a Mackay icosahedral Fe_{55} core with a shell-by-shell growth pattern. The surface of the Fe_{55} core is protected by twelve $P\mathit{t}Bu_3$ and forty-six hydrides. The [Fe_{55}] can be viewed as a transitional species in geometric structure from small cluster complexes to large nanoparticles. The anionic [Fe_6] shows an octahedral core, which is protected by six silylamides (*i.e.*, $-N(SiMe_3)_2$) and eight hydrides. The molecular formulae of [Fe_{55}] and [Fe_6] were studied by electrospray ionization mass spectrometry (ESI-MS). Theoretical analysis was performed to study the plausible locations of surface hydrides on [Fe_{55}][Fe_6]. X-ray absorption fine structure (XAFS) was also performed on [Fe_{55}][Fe_6] in order to uncover the oxidation state of Fe atoms and average coordination numbers. Finally, magnetism in [Fe_{55}][Fe_6] was characterized by superconducting quantum interference device (SQUID), electron spin resonance (ESR) and Mössbauer spectroscopy. Overall, this work provides valuable information on atomically precise chemistry of Fe NCs.

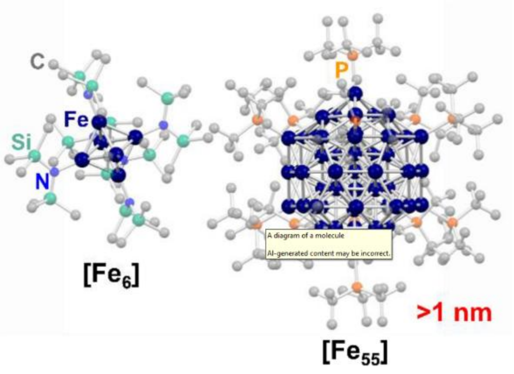

FIGURE 1. CRYSTAL STRUCTURE OF [FE_{55}][FE_6]. H ATOMS ARE OMITTED

Reference

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Molecular Alloy Carbonyl Nanoclusters

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Keywords: molecular nanocluster; carbonyl ligand; nanoalloy; X-ray diffraction; electrochemistry

Alloying metals in the nano and sub-nano domain is attracting an increasing interest from both a fundamental and applicative point of view.[1] Different chemical and physical properties may arise, and these can find several applications particularly regarding catalysis, biology, biomedicine and sensors.[2] From the structural perspective, alloying may occur randomly or in an ordered way.[3] In the latter case, "ordered" may correspond to site-specific doping, formation of well-defined ordered phases, segregation or related phenomena where the different metals occupy well defined positions. Often, in the real systems, intermediate behaviors between "random" and "ordered" are observed, that is, the different metals display a preference for some sites, but some level of disorder is present. In order to get an atomic insight into these phenomena, the study of perfectly defined molecular systems is required.[4]

Herein, we present some examples of Ni-Pt, Ni-Pd and Fe-M (M = Cu, Ag, Au) molecular alloy carbonyl nanoclusters, whose structures have been determined by single crystal X-ray diffraction (SC-XRD). The nature of these systems has been further elucidated by spectroscopic, electrochemical, spectroelectrochemical and computational methods.[5]

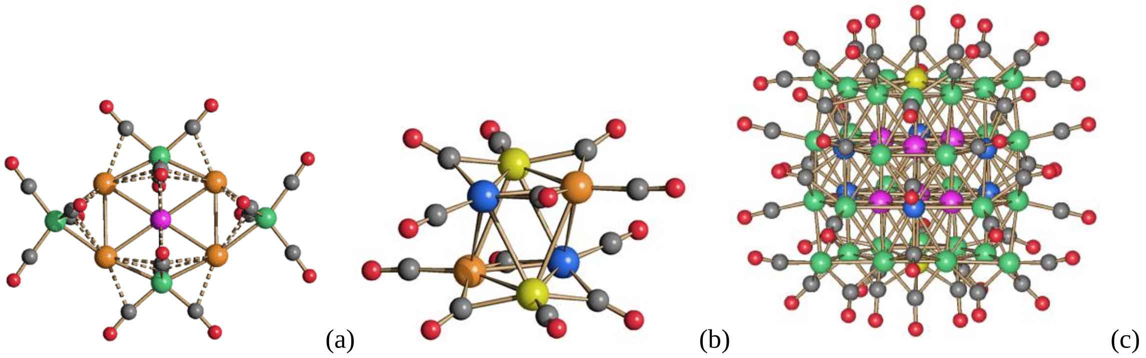

Figure. Molecular structures of (a) $[M_xM'_{5-x}Fe_4(CO)_{16}]^{3-}$ (x = 0-5; M, M' = Cu, Ag, Au; M ≠ M') (purple, M in the centre; orange, M in the corner positions; green, Fe; grey, C; red, O), (b) $[Pt_{6-x}Ni_x(CO)_{12}]^{2-}$ (x = 0-6) (yellow, blue and orange have been used for disordered Ni/Pt positions; red, O; grey, C), and (c) $[Ni_{37-x}Pd_{7+x}(CO)_{48}]^{6-}$ (x = 0.69) (green, Ni; purple, Pt, yellow, Ni/Pd ≈ 33:67; blue, Ni/Pd ≈ 91:9; grey, C; red, O).

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Electronic structure of ligated atom-precise noble metal superatoms and supermolecules

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Keywords: Nanoclusters, stability rules, encapsulated hydrides.

Superatoms are compact clusters of spheroidal shape, the electronic structure of which can be related to that of polyelectronic atoms.1 As for simple atoms or atomic ions, chemical stability of superatoms is most often reached when they satisfy the closed-shell requirement ("magic" number of valence electrons). Isolable atom-precise closed-shell noble metal superatoms are protected by a peripheral shell made of ligands and possibly additional metal centers in the d10 configuration.

In a similar way, as unstable open-shell atoms can bind together to form stable closed-shell molecules, open-shell superatoms can also assemble to form ligand-protected closed-shell "supermolecules".2 As for molecules, closed-shell stability (octet rule, for example) is also most often required for such assemblies of superatoms.

In this presentation we analyze the electronic structure of stable ligated noble metal superatoms,3 and explain why some of them do not follow the regular superatom electron counting rules. "Supermolecules" made of several superatoms are also considered and predicted to be stable entities, which are the counterparts of molecular systems such as I3-, I42-, SF2 or CO2.4

Particular attention will be paid to clusters encapsulating hydrides in which hydrogen behaves in some way as an interstitial dopant. The electron of an encapsulated hydrogen atom contributes to the "magic" electron count (n+1), whereas the opposite situation occurs in the case of an ordinary peripheral hydride, i.e. (n-1).5 The dynamics of these particular hydrides inside the cluster core has also been investigated.

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Bonding architecture of delocalized bonding in clusters and intermetallic compounds from DR analysis

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In many clusters the number of diatomic bonding contacts counted exceeds the number of orbitals available for this purpose. These cases are often ascribed to an unspecified general delocalized multicenter bonding scenario with an overall number of cluster bonding orbitals or electrons being related to some prototype cluster model. A finer characterization of the local bonding situations of its constituents and their synergistic cooperation (bonding architecture) is often missing although it may be considered to represent the decisive result for chemical understanding of these systems and building bridges to crystalline intermetallic phases with 3D networks. There are only a few methods available that claim to allow analysis of multicenter bonding architectures on the basis of first principles DFT calculations. The challenge in developing such a methodology lies in the effort to avoid preconception bias as much as possible. Nevertheless, as the final step calibration of the methodology is mandatory.

Closo-boron hydrides $\mathrm{B}n\mathrm{H}n2–$ (n = 5 to 12) and related clusters are a conceptually well understood class of compounds [1,2] suitable for calibration studies of new methodologies. For these and a few related prototype compounds, both the local and the global picture of 3-center bonding are extracted from position-space quantities based on the electron density and the pair density. For this purpose, three-center delocalization indices between QTAIM (quantum theory of atoms in molecules) atoms in position space are used to develop a consistent set of local bond and triangle, and global cluster delocalization ratios (*DR*s) *G*, which are quantitatively compared to conceptual *G* values derived from the Lipscomb's [1] and TORI's (Topological Octet Rule Implementation) [3] *styx* code for each cluster [4]. Combination of the cluster *DR*s with associated effective numbers of skeletal electron sharing (*SES)* for selected cluster surface edges, triangles or the whole cluster yields effective *styx* type values describing the trend and even the size of the conceptual *styx* codes for *closo*-boranes $\mathrm{B}n\mathrm{H}n2–$ and related systems with increasing cluster size *n* reasonably well [4]. For non-uniform cluster topologies, the different vertex degrees are shown to cause systematic 3-center wise bond delocalization effects for the associated edges and triangles of different average vertex degrees. Extension of DR analysis beyond the styx type triangular cluster-surface bonding corresponds to a triangulation of multicentric bonding. The cluster-wise results keep indicating consistency with the mixed 2- and 3-center bonding approach.

The successfully established chemical meaning of the local edge, triangle, and global cluster *DR*s and their associated *SES* values constitutes the basis for systematic investigations of mixed 2- and 3-center bonding scenarios in particular in intermetallic and related (endohedral) cluster compounds.

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Theoretical Analysis of Bonding and Electronic Structure of Heteroatom Doped Coinage Metal Superatomic Nanoclusters

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Keywords: Electronic Structure, Coinage Metal, Nanocluster, Superatom

Doping plays a pivotal role in modulating the bonding patterns and electronic structures of coinage metal superatomic nanoclusters, offering a versatile strategy to tailor their physicochemical properties. By introducing heteroatoms (e.g., Pd, Pt, or non-metal elements) into coinage metal (Au, Ag, Cu) nanoclusters, the geometric and electronic configurations undergo significant alterations. This study focuses on the theoretical investigation of bonding and electronic structure in heteroatom-doped M12 coinage metal superatomic cages. Results indicate that the valence electrons of certain dopants, such as W, Re, Os, Ir, Pt, and/or H, significantly contribute to the free electron count of the cluster and substantially alter its superatomic shell configuration. These tailored electronic structures impart distinct properties compared to their homometallic counterparts, advancing their applications in functional nanomaterial science.

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Modelling growth and dissolution of metallic copper cluster in the framework of nanoparticles chemistry

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Understanding of the reduction/nucleation/growth processes is a challenge to chemist, as it involves a large diversity of chemical and physical effects, a complex balance in the thermodynamic driving forces and various range of time scales for the kinetic behaviour. We have recently shown that combined DFT examination of the reduction steps and experimental speciation in the course of the synthetic process could shed light on the competition between reduction and disproportionation in the case of Cu(0) nanoparticles synthesis.[1] However, the high temperature required for the process did not allow us to understand the thermodynamic of the formation of the first clusters in solution. We next turned our attention a near-ambient temperature synthesic method based on the thermal decomposition of an alkyl copper reagent.[2] This decomposition reaction was long known[3] and the mechanism suggested involves two key steps: a β-hydride elimination forming a Cu-hydride intermediate, followed by reductive elimination yielding Cu(0). Kinetic studies suggested an autocatalytic mechanism involving mixed-valence Cu(I)-Cu(0) species, potentially catalytically active.[4] The Cu-hydride intermediate especially echoes to catalytically active Cu nanocluster invoked in the hydrosilylation of benzaldehyde.[5] Indeed, both processes have in common the formation of mixed Cu(0)xCu(I)yHz clusters which can either grow (Cu NPs formation) or shrink (catalytic conditions). The two processes can thus be considered as opposite directions of a single equilibrium, which can be schematically written as (R = alkyl or sillyl) :
Cu(I)-R + Cu(0)xCu(I)yHz D Cu(0)x+2Cu(I)y-1Hz-1 + R-H
We have examined computationally this reversible redox process and evidenced how the size of the cluster and the nature of the ligands stabilizing the intermediates and product can alter its kinetic and thermodynamic features.

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Polymer-Based Delivery Strategy for Mo$_6$ Clusters Radio/Photosensitizers

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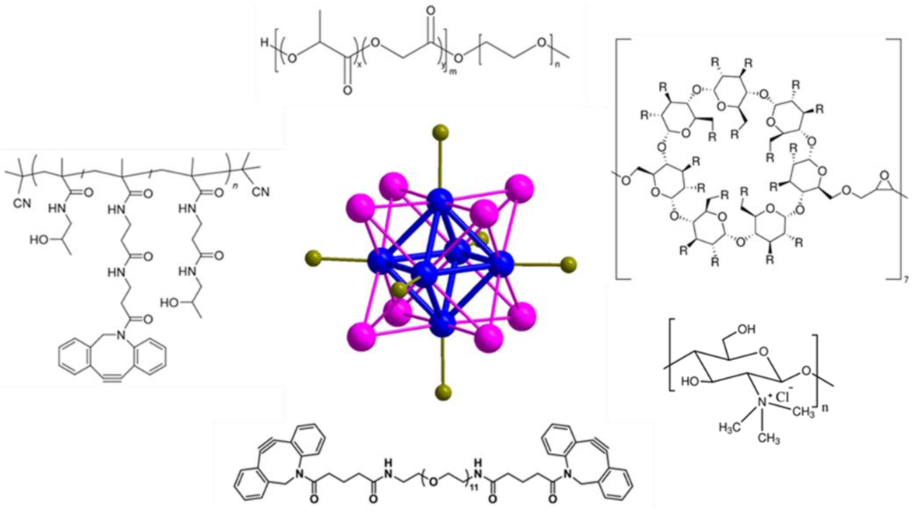
Octahedral molybdenum cluster (Mo$_6$) complexes are metallic aggregates stabilized by eight halogen inner ligands and six organic/inorganic apical ligands. Upon excitation with UV/blue-light or X-rays, these complexes display red phosphorescence and produce singlet oxygen, $O_2(^1\Delta_g)$ in high yields. Such properties have led to various applications in photodynamic therapy (PDT), photoinactivation of bacteria, or X-ray induced PDT [1]. However, direct administration of Mo$_6$ complexes is not pertinent owing to their insolubility or instability in aqueous medium. Herein, several strategies towards the use of organic polymer as delivery vehicles for Mo$_6$ complexes will be presented. Focus will be drawn on how the polymer nanocarrier enhances the photophysical and colloidal stability of Mo$_6$ complexes and mediates the cellular uptake, thus promoting the photo/radiotoxic effects.



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Nanocomposites based on metal atom cluster for light-driven applications

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Keywords : Transition metal atom cluster, hybrid polymers, phosphorescent nanocomposites, active soft materials

The combination of transition metal clusters (MC) with polymers allows the design easy-to-shape-functional materials with enhanced application versatility. $[(M_6L^i_8)L^a_6]^{n-}$ units (^{a} = apical, ^{i} = inner, M = Mo, Re, W; L = halogen, chalcogen, organic ligands)) constitutes the basic building block in the octahedral cluster chemistry and is easily obtained *via* high temperature solid state synthesis. The delocalization of valence electrons on the whole metallic scaffold of MC leads to unusual electronic, magnetic and optical properties. Concerning the optical properties MC show high emission in the red-NIR area and are able to generate singlet oxygen for applications in lighting, optoelectronics, sensors and photodynamic therapy. To take advantage of their intrinsic properties in applications and prevent self-aggregation, a careful choice of the host matrix and design of metal atom clusters is required.

Over the years we have developed various strategies in order to obtain homogeneous materials and in particular polymers nanocomposites maintaining the integrity of MC. [1]

In this presentation, these different strategies and the properties of the resulting hybrid polymers will be presented, in accordance to the best polymer matrix for the final application desired. MC have been embedded into polymethylmethacrylate (PMMA) [2], polyurethane (PU) [3], polyurea (PUR) [4] and polydimethylsiloxane (PDMS) [5] for lighting, reactive oxygen species generation, as solar concentrators and solar cells.

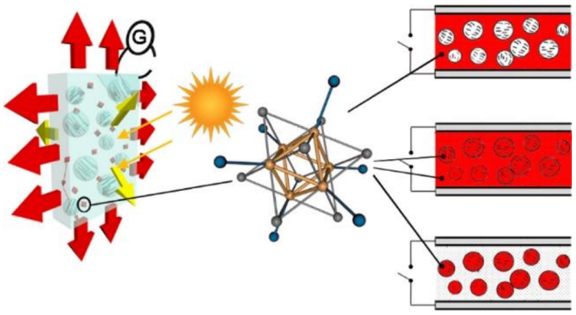

Figure1. Schematic representation of Mo cluster solar concentrator based on Polymer Dispersed Liquid Crystals technology.

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Molybdenum Cluster Nanoparticles for Radiodynamic Cancer Cell Therapy

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Keywords: RDT; Molybdenum clusters; Cancer therapy, Nanomedicine

Photodynamic therapy (PDT) is a promising strategy in cancer treatment, relying on the generation of cytotoxic reactive oxygen species (ROS) upon activation of photosensitisers by light. However, the limited tissue penetration of visible light restricts its effectiveness against deep-seated tumors. Radiodynamic therapy (RDT) has emerged as a complementary approach, using ionizing radiation to activate radiosensitizers and thereby overcome the depth limitations of traditional PDT. This study presents the development of a nanosystem based on an octahedral molybdenum cluster designed for RDT. In vitro evaluation was conducted using prostate adenocarcinoma (TRAMP-C2) cells. Upon irradiation with blue light (460 nm), the nanoparticles showed a potent phototoxic effect with an IC_{50} of 200 nM, while demonstrating no dark toxicity (>50 µM). This represents the most effective system we have developed to date. Light-activated treatment induced a substantial increase in intracellular ROS, consistent with oxidative stress-mediated cytotoxicity. The induced cell death displays features distinct from classical apoptosis or necrosis, indicating a potential non-canonical mechanism such as ferroptosis 1. Exposure to X-rays alone caused DNA damage in cancer cells, which did not significantly affect viability but impaired proliferation. When combined with molybdenum nanoparticles, X-ray irradiation led to a pronounced reduction in clonogenic survival, confirming a radiosensitising effect. These findings suggest that the nanoparticles not only enhance the therapeutic outcome but may also allow for a reduced radiation dose to achieve equivalent efficacy. Octahedral molybdenum clusters thus represent a versatile, dual-activation platform for both PDT and RDT. Their ability to be triggered by both light and ionising radiation makes them highly promising candidates for treating tumours located in deep or otherwise inaccessible tissues. Ongoing work is focused on translating these results into in vivo models to further assess therapeutic potential and inform future clinical strategies. This work was supported from the grant of Specific university research – grant No A2_FPBT_2025_053.

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Antibacterial Resins with Photoactive Octahedral Molybdenum Iodide Clusters

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Keywords: Molybdenum cluster, Photoluminescence, Reactive Oxygen Species (ROS), Resin, Antibacterial

The recent pandemic has increased interest within the scientific community in developing antimicrobial tools to maintain sensitive spaces as aseptically as possible. The integration of the photoactive $\{Mo_6I_8\}^{4+}$ cluster units into organic resins for antimicrobial applications presents a promising solution. In the presence of atmospheric oxygen and visible light, the molybdenum additive can produce singlet oxygen ($^1O_2$), a well-known reactive oxygen species (ROS), useful for photodynamic therapy and antibacterial applications. [1],[2] To enhance the cluster's efficiency as a $^1O_2$ generator, the Mo_6I_8 cluster core was decorated with organic ligands, thereby increasing the quantum yield.[3] The $\{Mo_6I_8\}^{4+}$ compounds were synthesized and used as an additive to be integrated with varying ratios into an organic polymeric resin. The molybdenum cluster-based resin was characterized through powder X-ray diffraction, optical (UV-visible, photoluminescence), ATR-FTIR and Raman spectroscopies, and scanning electron microscopy (SEM). Bactericidal tests were conducted for the Mo_6I_8 cluster-based resin with *Escherichia coli* and *Staphylococcus aureus* under irradiation with visible light. Optical measurements confirmed that the cluster maintains its photoactivity upon incorporation into the organic resin. Bactericidal assays indicated a direct correlation between cluster concentration and bacterial death. The hybrid resins proved to be robust and capable of decreasing the population of bacterial colony forming units by 99.9%.

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Surface Coordination Chemistry of Metal Nanomaterials

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Keywords: surface coordination chemistry, metal nanocluster, heterogeneous catalysis, selective hydrogenation, ligand effect

The surface and interface of solids is the place where many chemical reactions take place. How to achieve precise control of chemical reactions at solid surfaces and interfaces is a long-term challenge in heterogeneous catalysis. Although surface modification has been well documented as an important means to optimize heterogeneous catalysts, the mechanistic understanding of how surface modification manipulates heterogeneous catalysis is still severely lacking. In this presentation, we will discuss our ongoing research efforts to understand how the organic/inorganic coordinative species on metal surfaces manipulate their catalytic properties. Based on the development of new methods to construct model metal materials to resolve the molecular level structures of typical metal-organic and metal-support interfaces, we have elucidated the molecular mechanisms of related interfaces in catalysis from the perspective of coordination chemistry. The understanding has been successfully applied to optimize the chemical properties of metal nanomaterials for green chemistry. The coupling of the developed techniques with renewable electricity will be discussed too.

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Rearrangement of Surface Coordination Structures of Silver Nanoclusters and Its Influence on the Luminescent Properties of Nanoclusters

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Keywords: Silver Nanocluster, Surface Coordination Structures, Carboxylate Ligands, Luminescence, Structure-property relationship

The surface coordination structures of metal nanomaterials are closely associated not only with the metallic cores but also with the surface organic ligands. As a crucial sensitive layer that affects the overall properties of the materials, it has attracted extensive attention from researchers. Since the "staple" surface coordination structure (RS-Au-SR) of thiolate-protected gold nanoparticle was disclosed [1], the relevant research aimed at regulating the properties of coinage metal nanomaterials by rearranging their surface coordination structures has not been carried out effectively. The primary reason is that the Au-S bond in the "staple" surface coordination structure is relatively robust, and there exists metal-metal interactions between the surface Au ions and the inner Au atoms within the cluster core. When the surface coordination structure changes, the core of the metal nanomaterial will change correspondingly, which subsequently results in alterations to the overall structure and properties of the clusters [2]. Consequently, it is challenging to accomplish the rearrangement of the surface coordination structure, and as a result, it is difficult to elucidate the structure-property relationship between the surface coordination structure and the properties of the clusters.

Our recently studies focus on the carboxylate protected silver nanoclusters (RCO_2-AgNCs), which ligand has relatively weak coordination interaction with silver ions [3]. The rearrangement of the surface coordination structure of RCO_2-AgNCs was successfully accomplished. Specifically, the chemical compositions of the clusters were consistent, their core structures were identical, and only the surface coordination structures differed. By making a comparison and analysis of the structural differences and property variations of RCO_2-AgNCs, and combining DFT calculations and ultrafast absorption spectroscopy techniques, the mechanism by which the surface coordination structure affects the changes in the luminescent properties of RCO_2-AgNCs was revealed. These investigations clarify the relationship between the surface coordination structure and the luminescent properties of RCO_2-AgNCs, providing new ideas for the design of nano-optical devices with atomic precision.

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Reactivity of terminal ligands coordinated to octahedral M_6 cluster cores

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Octahedral rhenium- and molybdenum-based clusters are known to display interesting electrochemical and photophysical properties. In addition, their regular geometry and non-fluxional metal cores provide advantages in using these clusters as building blocks in the preparation of functional materials. Notably, the reactivity of these systems is limited in comparison to studies conducted on single metal complexes. Therefore, research in the Szczepura group has focused on developing synthetic methodologies for the preparation of rhenium chalcogenide and molybdenum halide clusters with a specific focus on expanding the breadth of terminal ligands bonded to these discrete cluster cores. Studies include investigation into the reactivity and physical properties displayed by these clusters with particular interest in detailing differences in reactivity of ligands bonded to single metal centers vs these hexanuclear cluster cores. Our most recent studies have focused on the coordination of C-donor ligands, such as N-heterocyclic carbenes and phenylacetylide ligands, to the [Re6Se8]2+ cluster core. This presentation will discuss the synthesis and reactivity of these organometallic clusters and will also provide an overview of key findings regarding the impact of M6 cluster cores on the reactivity of coordinated (terminal) ligands.

Activation of H-H and H-Si Bonds Using Molybdenumn Sulfide Cluster Catalysts

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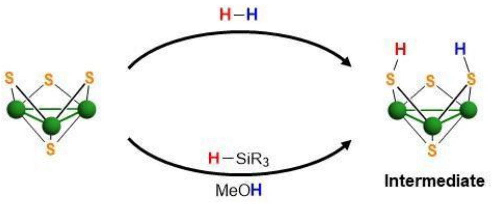
Keywords: Cluster Catalysis, Molybdenum Sulfides, Hydrogenation, Methanolysis, Reaction Mechanisms

Incomplete cubane-type Mo_3S_4 clusters share structural features with the MoS_2 basal planes, and can serve as molecular models of the active sites of this heterogeneous catalyst. Our group has shown that these Mo_3S_4 complexes, are efficient catalysts for the hydrogenation and silane transfer hydrogenation of nitro- and azoarenes to produce anilines.[1-2] In this presentation, the catalytic performance of these complexes for the (Z)-selective semihydrogenation of internal alkynes, hydrogenation of sulfoxides to sulfides and methanolysis of silanes will be analyzed.[3-5] Our results support the operation of a sulfur- centered reaction mechanism for the hydrogen H-H and hydrosilane H-Si bond activation to afford a bis(hydrosulfide) intermediate, as represented in the figure:



Once the $Mo_3(\mu_3\text{-}S)(\mu\text{-}S)(\mu\text{-}SH)_2$ intermediate is formed, hydrogen is transferred to the organic substrate, alkyne or sulfoxide, or released in the case of the methanolysis of hydrosilanes. Special emphasis will be given to the reaction mechanisms of these transformations. All our mechanistic proposals are framed as cluster catalysis and based on a combined experimental and theoretical approach.

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Photocatalytic Potential of Octahedral Molybdenum Clusters: From Design to Application

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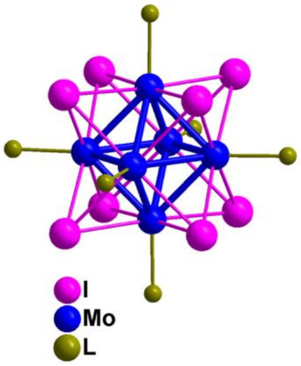
Keywords: Molybdenum cluster; Reactive oxygen species; Bacterial photoinactivation; Pollutant degradation

Octahedral molybdenum cluster complexes (Mo_6) are promising materials for photofunctional applications due to their photostability and oxygen-sensitive red phosphorescence. These complexes efficiently generate singlet oxygen, $O_2(^1\Delta_g)$. The tunability of their properties through ligand modification allows for further functionalization, positioning Mo_6 complexes as candidates for use in photodynamic and radiodynamic therapy, antibacterial photoinactivation, and photocatalytic degradation of pollutants [1].

This research explores the potential of Mo_6 chemistry in two key areas: bacterial photoinactivation and pollutant degradation. We present the mechanisms responsible for the formation of reactive oxygen species (ROS). We developed Mo_6-based functional layers capable of photodynamically inactivating biofilms. These materials leverage the unique ability of Mo_6 sensitizers to produce $O_2(^1\Delta_g)$ even in the solid state, enabling the fabrication of simple, single-component active layers [2]. We further compare the photoactivity of these layers to that of Mo_6-based composites, specifically $Mo_6@CeO_2$ and Mo_6@graphene oxide. In these composites, the typical singlet oxygen generation pathway is bypassed. Instead, a fast photoinduced electron transfer occurs from the excited triplet state of Mo_6 to the conduction band of the semiconductor component leading to the release of ROS [3,4]. As a result, this mechanism significantly enhances the photocatalytic degradation of the endocrine disruptor bisphenol-S under UV-A irradiation.



By correlating the morphology, composition, and phosphorescence characteristics of these Mo_6-based materials with their ROS production, antibacterial performance, and photocatalytic efficiency, we identify the key factors that influence their overall activity. This study underscores the potential of Mo_6-based composites as advanced photooxidative materials.

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Clusters-polyoxometallates eco-compatible tandems for the production of hydrogen: from molecular assemblies to the device

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Keywords: Solar hydrogen production, photoelectrocatalytic systems, metal atom cluster, polyoxometallates, photoelectrode

Green hydrogen, as an energy vector, holds the promise of a clean, cheap and sustainable energy. However, the development of green and efficient photo-induced hydrogen catalytic systems for hydrogen evolution reactions (HER) implies to consider their chemical compositions. The most efficient systems reported in the literature contain noble metal like ruthenium or iridium as sensitizers, and they suffer from their lack of stability that originates from the photo-bleaching of organics components. In that frame, we are currently investigating greener systems, free of noble-metal or toxic elements, as photoelectrocatalytic systems for solar hydrogen production. They associated metal atom clusters (CLUS) and polyoxometallates (POMs) to form push-pull tandems, namely CLUSPOMs. In the CLUSPOMs tandems, the cluster building blocks $[M_6L^i_8L^a_6]^{2-}$ (M=W, Mo; L=Ligands) acts as a robust photosensitizer. These are electron-rich molecular entities exhibiting very interesting optical properties such as phosphorescence in the NIR region triggered by UV-visible radiations with hundreds of microseconds lifetime[1][2] making them suitable for photocatalytic applications. Polyoxometallates (POMs) are water-soluble metal-oxide discrete polyanions (e.g. $[P_2W_{18}O_{62}]^{6-}$ and $[PW_{12}O_{40}]^{3-}$), displaying the ability to exchange reversibly several electrons, making them highly relevant for catalytic processes involving multi-electrons transfers. Sulfur-functionalized POMs (i.e. $[AsW_{15}O_{53}Mo_3S_4(H_2O)_3]^{7-}$ and $[(PW_{11}O_{39})Mo_3S_4(H_2O)_3OH]^{8-}$), namely polyoxothiometallates, are proven to be among the most efficient POM-based HER photoelectrocalaysts so far reported in the literature[3][4]. The association of cationic clusters and anionic POMs offers the prospect of the development of new high-performance all-inorganic photoelectrocatalytic systems for hydrogen production. In this talk, we will present the first steps of the design and the characterization of cationic cluster-based photoelectrodes. In particular, we will expose how to control the composition of the cluster-based films to reach cationic anchoring groups to associate anionic POM and build in the CLUS-POM architectures.

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Atomically precise palladium clusters and nanoparticles as catalysts for hydrogen production and hydrogenation reactions using organocobalt complexes

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The efficiency of atomically-precise nanoclusters in catalysis is a key to understand the detailed mechanism of catalytic mechanisms in nanoclusters and on surfaces. Here, the kinetics of several palladium nanoclusters and nanoparticles in hydrogen production and transfer hydrogenation of olefins with organocobalt complexes have been studied. In this communication, the kinetics and efficiency of several palladium nanoclusters will be compared with those of ligand-poor palladium nanoparticles. This work should improve the knowledge and understanding of mechanisms in nanocatalysis.

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Nanocluster Catalysis: Breaking Conventions Through Machine Learning and Artificial Intelligence

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Nanoclusters are pivotal catalysts due to their high surface area and distinct structure-activity relationships. However, conventional approaches often center on larger clusters, overlooking the unique catalytic behaviors of smaller, subnanometer clusters. Recent findings demonstrate that the atomicity of these clusters can dramatically influence their catalytic properties, with even a single atom modification causing significant changes in activity. This talk will explore how machine learning is transforming our understanding of nanocluster catalysis, particularly in examining electronic structures and the impact of external factors. We will also showcase our work on applying machine learning to optimize the catalytic performance of platinum-based nanoclusters in the oxygen reduction reaction (ORR), with a focus on the critical roles of atomicity and relativistic effects.[1-7]

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Unraveling the Role of Orbital Interaction in the Electrochemical HER of the Trimetallic AgAuCu Nanobowl Catalyst

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Keywords: Electrocatalyst; Nanobowl; AuAgCu; HER; Orbital Interaction.

Unraveling the origins of the electrocatalytic activity of composite nanomaterials is crucial but inherently challenging. Here, we present a comprehensive investigation of the influence of different orbitals' interaction in the AuAgCu nanobowl model electrocatalyst during the hydrogen evolution reaction (HER). According to our theoretical study, AgAuCu exhibits a lower energy barrier than AgAu and AgCu bimetallic systems for the HER, suggesting that the trimetallic AgAuCu system interacts optimally with H*, resulting in the most efficient HER catalyst. As we delve deeper into the HER activity of AgAuCu, it was observed that the presence of Cu allows Au to adsorb the H* intermediate through the hybridization of s orbitals of hydrogen and s, $dx^2–y^2$, and dz^2 orbitals of Au. Such orbital interaction was not present in the cases of AgAu and AgCu bimetallic systems, and as a result, these bimetallic systems exhibit lower HER activities.

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Graphene Decorated with Mo_3S_7 Clusters for Gas Sensing

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Keywords: Molybdenum sulfido cluster, graphene, gas detection, resistive sensor

Developing highly sensitive and selective sensors based on sustainable materials has been the subject of intensive research in recent years. Inexpensive and low-toxic nanomaterials, which can be operated under room temperature conditions, are now gaining momentum for developing low-power and unattended sensing networks. Specifically, Earth-abundant transition metal cluster compounds are suitable candidates due to their characteristic properties halfway between metal nanoparticles and metal coordination complexes. Recently, hexametallic molybdenum clusters with halides supported onto graphene have been explored for gas detection [1], [2]. Regarding lower nuclearity molybdenum clusters, while materials based on trinuclear molybdenum sulfido clusters have attracted significant attention for their applications in photo and electrocatalysis, their sensing behavior toward gases is still incipient [3].

In this communication, cutting-edge research on the sensing ability of the $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_2)_3]^{4+}$ cluster units, with chlorides and coordinatively supported on graphene, towards harmful and toxic gases such as molecular hydrogen, carbon monoxide, carbon dioxide, and benzene, is presented. This hybrid material was prepared and characterized by spectrometric, textural and X-ray based techniques. Using an electrical transducing scheme, we have developed a unique device based on a Mo_3S_7@Graphene nanohybrid and we have studied its performance for detecting these different air pollutants. For a better understanding of its behavior, plausible sensing mechanisms and computational studies are discussed. The results show an outstanding chemoresistive sensing performance towards CO_2, with excellent stability and repeatability. For the first time, molybdenum sulfido composites have been employed to detect CO_2. Besides, the sensors developed are aligned with the need to develop affordable CO_2 sensors for environmental sustainability.

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Enigmatic formation of hydrogen peroxide from molecular hydrogen by human metalloenzymes

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Keywords: molecular hydrogen, hydrogen-rich water, peroxidases, redox signaling

Molecular hydrogen (H_2) is not only a promising fuel for a green economy but also serves as both a substrate and product of anaerobic bacterial metabolism in the human intestine. Until 2007, H_2 was considered biologically inert in human cells and enzymes. However, its antioxidant properties were subsequently reported, sparking extensive research [1]. Since then, thousands of studies have described the broad biological effects of H_2 on mammalian systems, including anti-inflammatory, anti-diabetic, and regenerative effects—though the underlying mechanisms have remained unclear. Here, we report for the first time that H_2 can react with molecular oxygen (O_2) on human oxidoreductase metalloenzymes, producing reactive oxygen species in the form of hydrogen peroxide (H_2O_2). H_2O_2 is a potent signaling molecule, and its enzymatic generation may help explain the observed physiological effects of H_2 in humans. We show that both heme-iron–containing enzymes and iron–sulfur (Fe-S) cluster–containing enzymes catalyze this reaction, whereas enzymes lacking iron do not. Nevertheless, the precise reaction mechanism remains unresolved, and we welcome insights from the scientific community. In conclusion, we identify a novel, fundamental source of the signaling molecule H_2O_2 in the human body, revealing a potential molecular link between gut microbiome metabolism and human health.

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Visible-Light-Driven Degradation of Phenolic Compounds by $Mo_6I_{12}/g\text{-}C_3N_4$ Systems

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Keywords: Photocatalysis, pollutant degradation, molybdenum cluster, carbon nitride.

The presence of phenolic compounds in water presents a serious environmental problem due to their high toxicity, persistence, and low biodegradability [1]. These issues underscore the urgent need for sustainable and efficient materials capable of addressing water contamination through environmentally friendly technologies. Photocatalysis is a clean technology that, through solar light excitation of a semiconductor, generates electron-hole for producing reactive oxygen species (ROS) to degrade organic pollutants in solution [2]. However, it presents several challenges, such as limited efficiency under low- light conditions, the potential for photocatalyst deactivation, and the need for expensive or scarce materials in some photocatalytic systems [2]. Octahedral Mo_6 halide clusters exhibit intense absorption in the visible region and possess rich redox chemistry, enabling efficient photoinduced electron transfer processes [3]. It is possible that, combined with carbon nitride ($g\text{-}C_3N_4$), a stable metal-free semiconductor with a suitable band gap and excellent chemical resistance [4], the resulting hybrid system facilitates synergistic charge separation and ROS generation under mild conditions. This makes $Mo_6I_{12}/g\text{-}C_3N_4$ system as promising materials for the photocatalytic degradation of persistent organic pollutants in water. In this work, we present a hybrid photocatalytic system based on Mo_6I_{12} supported on exfoliated carbon nitride nanosheets ($g\text{-}C_3N_4$), designed to efficiently degrade phenolic species under visible light irradiation. The resulting and stable heterogeneous material shows good dispersion of Mo active sites. Structural and optical characterization of the hybrid system was carried out using XRD, Raman, FTIR, UV-Vis, XPS, and SEM, confirming effective interaction between the two components. Photocatalytic tests were conducted in aqueous phenol, 4-chlorophenol, and bisphenol-S solutions as model pollutants, and degradation kinetics under visible light were evaluated using HPLC. The $Mo_6I_{12}/g\text{-}C_3N_4$ system showed enhanced activity compared to the individual components, attributed to the synergistic effect between the visible-light absorption of the cluster and the efficient charge separation facilitated by the semiconductor support. This study highlights the potential of molybdenum cluster–based hybrid metal–semiconductor materials as efficient and sustainable photocatalysts for the remediation of water contaminated with persistent organic pollutants.

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Probing the fluorescence intermittency of single metal nanoclusters

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Keywords: Nanoclusters, Gold, DNA origami, Single-molecule fluorescence.

Abstract: Noble metal nanoclusters connect the atomic and nanoparticle (plasmonic) domains. Because of their ultrasmall size, they exhibit significant quantum confinement effects, resulting in molecule-like capabilities such as discrete energy levels, electrical, and optical properties such as light emission and absorption.[1] Gold nanoclusters (Au NCs) have become innovative fluorescent nanomaterials due to their superior performance over organic dyes and semiconductor quantum dots in several areas, including biocompatibility, photostability, water solubility, and non-toxicity.[2] In addition, bimetallic NCs are essential for advancing various applications, due to their unique properties such as enhanced catalytic activity, improved optical characteristics, and increased biocompatibility compared to monometallic counterparts. To unravel the intricate dynamics of complex multi-component structures, single-molecule techniques have become a significant advancement over traditional ensemble average measurements.[3] Precisely doped metal NCs are of great interest as they possess unique photophysical properties because of the strong structure-property correlation. Both ensemble and single-molecule measurements were performed to explore the fluorescence properties of Au nanoclusters and Au doped Ag NCs.[4] We will include a discussion on the synthesis of DNA origami templated single Au NC at site-specific position and explored the phenomenon of fluorescence intermittency or blinking of individual Au NC assembled on DNA origami structures.[5] We also investigate the photophysical properties of DNA-templated bimetallic NCs, analysing their excited state dynamics and lifetimes.

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Emissive hybrid organic-inorganic nanocomposites integrating octahedral M_6 nanoclusters

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Keywords: hybrid materials; luminescence; supramolecular chemistry; metal clusters; optical writing; functional polymers; anticounterfeiting.

We report a series of multifunctional hybrid materials combining organic fluorophores—such as tetraphenylethylene- and anthracene-based derivatives—with red to near-infrared phosphorescent metal clusters such as the $[(M_6L^i_8)L^a_6]^{n-}$ cluster units (^{a} = apical, ^{i} = inner, M = Mo, Re, W; L = halogen, chalcogen, organic ligands)). These hybrids are constructed *via* modular strategies involving ionic exchange, hydrogen bonding, and copolymer embedding within polymer matrices like PMMA or PDMS. Their emission properties, investigated in both solution and solid state, exhibit remarkable tunability based on crystal structure, excitation wavelength, and environmental oxygen concentration.

These systems demonstrate a broad range of advanced photonic functionalities: UV-2A erasable optical writing, white-light waveguiding through hybrid microfibers, and inkless, rewritable printing with oxygen-sensitive emission modulation. Our results highlight the potential of supramolecular chemistry to engineer dynamic luminescent materials tailored for data storage, integrated optics, and anticounterfeiting technologies.

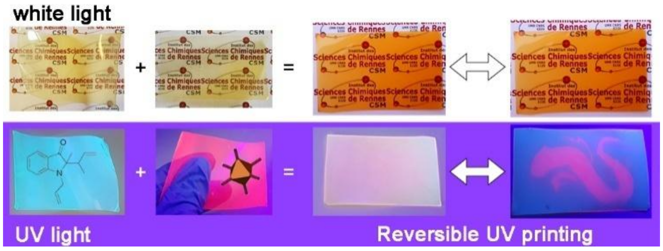

Figure 1. Doped polymers under sun light and UV light. From S. Khlifi *et al.*, *Mater. Today* **2020**, *35*, 34-41.

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Generation of Orbital Magnetism by Light in Atomically Precise Metal Clusters

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In view of the recent increased interest in light-induced manipulation of magnetism in nanometric length scales nanoparticles[1] and two-dimensional nano-domains[2] are emerging as potential materials of choice. With this emerges one of the fundamental question: how does the miniaturization of these systems impact the underlying physics. To this end, this ab-initio theoretical work presents metal clusters as promising elementary units for generating all-optical ultrafast magnetization. Within the real-time (RT) formalism of time-dependent density functional theory (TDDFT), simulation of plasmon excitation in atomically precise clusters using circularly polarized laser pulse captured the transfer of angular momentum from light field to induce orbital magnetic moment. In the near-field analysis, the origin of the orbital magnetization is traced back to the self-sustained circular motion of the induced electron density which corroborates the presence of nanometric current loops giving rise to orbital magnetic moments. The results[3] provide valuable insights into the quantum many-body effects that influence the light-induced orbital magnetism in metal clusters depending on its geometry and chemical composition. At the same time, they explicitly demonstrate the possibility for harnessing magnetization in metal clusters, offering potential applications in the field of all-optical manipulation of magnetism.

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Octahedral Metal Cluster-based Building Blocks: Towards the Engineering of New Ambipolar Photoelectrodes for Solar Energy Conversion

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Keywords: Octahedral Metal Clusters, Photoelectrodes, solar energy conversion, ambipolarity

Ambipolar materials are a class of compounds that can intrinsically transport and transfer simultaneously both charge carriers, holes and electrons in a comparable way [1]. Unlike conventional unipolar semiconductors in which a type of charge carrier is predominant, ambipolar materials can display p-type and n-type characteristics, which makes them attractive materials for many different application fields such as sunlight conversion [2,3]. Only few materials such as semiconducting polymers, carbon nanotubes, 2D materials or organic-inorganic hybrid perovskites exhibit ambipolar behaviors [1,3]. Their intriguing intrinsic physical properties result from their specific electronic structures that are not only related to the chemical compositions but also to morphology and size effects [1,3].

Recently, we have completed this family of materials by a new series of compounds, namely the transition metal cluster (MC) compounds based on Mo_6, Re_6, and mixed $(Mo,Re)_6$ clusters [4,5,6]. $[\{M_6(Q,X)^i{}_8\}L^a{}_6]$ (M = Mo or Re, Q = S or Se, X = I and L = Cl, I or H_2O) cluster-based building blocks have a nanosize scale restriction giving them fascinating optical and electronic properties such as molecule-like energy gaps, strong absorption in the visible and/or NIR spectral regions, deep red luminescence or high (photo)catalytic effectiveness [4-8]. They are particularly well suited for nanoarchitectonics [4,5,6,9] whose the concept is based on the assembly of nanoscale units to reach new original physical properties. The design of photoelectrodes built on cluster core building blocks will thus be presented in this communication. The control of their composition and design led to the development of new ambipolar photoelectrodes with tailored optoelectronic properties. Beyond the deposition route, the origin and the engineering of the photoconductivity properties of MC-based layers will be discussed before to consider their interest as new light-harvesting layer for the solar energy conversion.

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Next Level Superatomic Materials

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The assembly of nanoscale building blocks offers exciting new avenues to create materials in which structure and functions can be chemically designed and tuned. In this context, the synthesis of inorganic molecular clusters with atomically defined structures provides a rich family of functional building elements. This presentation will describe our efforts to assemble such “designer atoms” into a variety of hierarchical structures in which the preformed clusters emulate the role of atoms in traditional atomic solids. The resulting materials offer a unique opportunity to combine programmable building blocks *and* atomic precision. As such, they bridge traditional crystalline semiconductors, molecular solids, and nanocrystal arrays by synergizing some of their most attractive features. Recent synthetic advances underpinning this concept will be presented, alongside the unique collective material properties that arise. In particular, I will discuss the synthesis of a novel two-dimensional superatomic carbon allotrope—graphullerene—and the emergence of acoustic polarons in the van der Waals superatomic semiconductor $Re_6Se_8Cl_2$. These acoustic polarons travel quasi-ballistically, a transport mechanism that diverges from traditional diffusive behavior and holds promise for next-generation solar energy conversion and lossless microelectronics.

Tuning Redox Potentials of Hexarhenium Complexes

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Keywords: Hexanuclear rhenium clusters, Redox potential, Luminescence

The study reports that the ground- and excited-state $\mathrm{Re_6(23e)/Re_6(24e)}$ redox potentials of an octahedral hexanuclear rhenium(III) complex can be controlled by systematically changing in the number and type of the *N*-heteroaromatic ligand (L) and the number of chloride ions at the six terminal positions. A series of octahedral hexanuclear rhenium complexes $[\mathrm{Re_6}(\mu_3\text{-S})_8\mathrm{Cl}_{6\text{-}n}(\mathrm{L})_n]^{n-4}$ (n = 1, L = 4-dimethylaminopyridine (dmap), 3,5-lutidine (lut), 4-methylpyridine (mpy), pyridine (py), 4-phenylpyridine (ppy), 4,4′-bipyridine (bpy), 4-cyanopyridine (cpy), and pyrazine (pz); n = 2, L = dmap, lut, mpy, py, 1,2-bis(4-pyridyl)ethane (bpe), ppy, bpy, cpy and pz; n = 3, L = lut, py, and bpy) was synthesized, and their redox and luminescent properties were investigated. The $\mathrm{Re_6(23e)/Re_6(24e)}$ oxidation potentials were linearly correlated with the pK_a of the *N*-heteroaromatic ligand [pK_a(L)], the ^{1}H NMR chemical shift of the ortho proton on L at the terminal position, and the Hammett constant (σ) of the pyridyl-ligand substituent. The series of the complexes showed a linear correlation with the sum of the Lever electrochemical parameters at the six terminal ligands. The complexes showed luminescence, and the photoemissive excited states of the complexes were assigned to the cluster core-centered excited triplet state (^{3}CC) or the metal-to-ligand charge-transfer excited triplet state (^{3}MLCT). The emission properties were dependent on the type of L coordinating at the terminal position. The ground- and excited-state oxidation potentials of the hexanuclear rhenium complexes can be finely tuned by the combination of halide and L ligands at the terminal positions.

The pz and bpy bridged $\{\mathrm{Re_6(24e)}\}_2$ dimers, $[\{\mathrm{Re_6}(\mu_3\text{-S})_8\mathrm{Cl_5}\}_2(\mu\text{-L})]^{6-}$ were synthesized. The cyclic voltammograms showed two-step of one-electron redox processes attributable to $\mathrm{Re_6(23e)Re_6(24e)}/\{\mathrm{Re_6(24e)}\}_2$ and $\{\mathrm{Re_6(23e)}\}_2/\mathrm{Re_6(23e)Re_6(24e)}$, respectively. The results suggest weak electronic interaction between two cluster units bridged by pz or bpy in the inter-cluster mixed valence state. The compounds show photoluminescence in the near-infrared region at 296 K in the solid state.

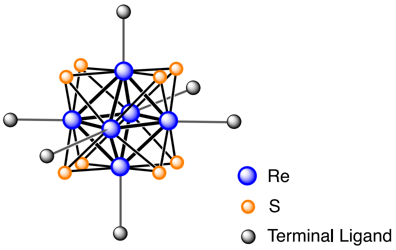

Fig. 1. Structure of the hexarhenium complex.

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A Journey into Super-Reduction of Wells-Dawson polyoxotungstate: Electron Storage in Metal–Metal Bonds

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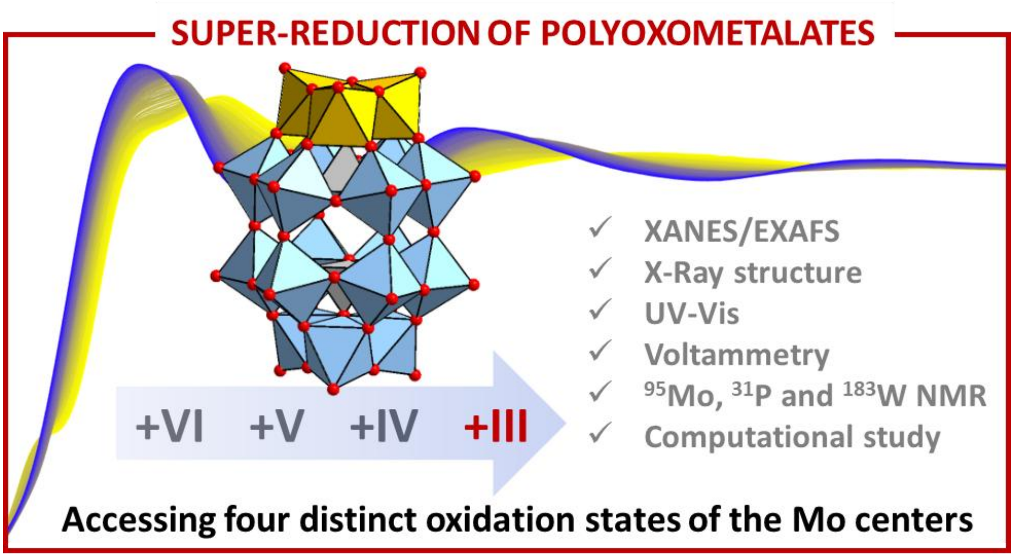
Keywords: Polyoxometalates – Electron reservoir – Metal-Metal bonds

Polyoxometalates (POMs) represent an extensive class of anionic molecular oxides of early transition metals recently identified as appealing redox mediators for applications in decoupled water-splitting systems, electro-organic synthesis, and redox-flow batteries. [1–3] Although POMs can be strongly reduced during the functioning of such electrochemical systems, the electron-storage mechanism within POMs remains poorly understood. In context, the first key challenge concerns the structural elucidation of super-reduced species, and the second one consists of discovering the potential structure-reducibility relationships.

Our research group has recently demonstrated that several POMs can store massively electrons within metal-metal bonds. [4-5] In this communication, we will unveil the mechanism of the super-reduction of Dawson-type POMs in an acidic solution. This presentation will be supported by i) in-situ measurements (XANES/EXAFS, UV-vis, and voltammetry), ii) ex-situ measurements (^{31}P and ^{183}W NMR, single-crystal X-ray diffraction), and in-silico studies.



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Reactivities of Copper Hydride Clusters with Terminal Alkynes: En Route to 2-Electron Superatom

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Keywords: coinage metals, hydride, superatom, crystallography

The Liu group has made a significant contribution to the synthesis and structural characterization of dichalcogenolate-stabilized copper hydrides since 2013. Some notable examples, including Cu32H20, Cu28H15, and Cu20H11, studied by single crystal neutron diffraction, were thoroughly discussed in a personal account.[1] Further reactions of Cu28H15 with terminal alkynes, first yielded Cu15H2,[2] then a 2e copper superatom, [Cu13(S2CNR2)6(C2Ph)4]+ possibly through a thermally induced internal redox reaction.[3] Intriguingly smaller copper hydrides, [Cu11H2(S2PR2)6(C2Ph)3],[4] can be isolated starting with Cu20H11, which was subsequently utilized to create 2e superatomic alloys, AgCu12 and AuCu12.[5] The latter alloy is highly emissive and exhibits orange-red photoluminescence at ambient temperature with 79% quantum efficiency observed for [AuCu12(dtp)6(C2C6H4F)4]+. Whereas Cu12H2 can be synthesized via inserting one Cu(I) ion into Cu11H2, only Cu8H and HC=CR were identified spectroscopically in the thermal treatment of Cu12H2. In the presence of Pd(II)/Pt(II) salts, the reactions of various copper hydrides with phenylacetylene yield a series of bimetallic copper-rich nanoclusters, [MCu14H2(dtc/dtp)6(C2Ph)4] (M = Pd(0), Pt(0)), encapsulating a linear [MH2]2- unit.[6, 7] Synthetic details focusing on the potent reducing ability of interstitial hydrides will be given in this presentation.[8]

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Exploring the Structure–Property Relationships in Transition Metal Clusters (Nb_6, Ta_6, Mo_6) for Energy Applications

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Keywords : Absorption, UV-NIR blocking properties, Structures, Conductivity

Octahedral M_6 transition-metal clusters coordinated by halide ligands can adopt edge-bridged or face-capped geometries. Their physical properties are strongly influenced by the metal identity, valence electron counts, and the nature of both inner (L^i) and apical (L^a) ligands. Despite being discovered over a century ago, these clusters continue to raise fundamental questions, as the intricate relationships between their structure, electronic configuration, and properties remain not fully understood. Their rich redox behavior, photophysical features, and potential for multifunctionality make them enduring subjects of interest across solid-state chemistry and materials science.

In the first part of this presentation, we investigate the physicochemical behavior and potential applications of hexanuclear halide clusters based on the $\{M_6X_{12}\}^{4+}$ core (M = Ta, Nb; X = halide)[1,2]. A combined experimental and computational study reveals how ligand substitution, solvent effects, and oxidation states influence the structural, optical, and redox properties of these clusters in both solid-state and solution. These findings were applied to design composites embedding $[\{M_6X^i_{12}\}X^a_{6-x}(H_2O)_x]$ in a polyvinylpyrrolidone (PVP) matrix for energy-saving glass coatings. The resulting nanocomposites, particularly for M = Nb and X = Cl, exhibit outstanding UV and NIR blocking properties (>90%) with high visible transparency, reaching a figure of merit (FOM) of 1.29 - positioning them among the best-performing materials for solar control applications.

In the second part, we explore molybdenum cluster-based materials $(H)_4[Mo_6Br_6S_2(OH)_6]\cdot 12H_2O$ and $(H)_2[Mo_6X_8(OH)_6]\cdot 12H_2O$ (X = Cl, Br)[3], which display both luminescence and significant proton conductivity. The latter arises from extended hydrogen-bond networks and shared protons between clusters, as confirmed by ab initio molecular dynamics simulations. Our combined experimental-theoretical approach reveals a Grotthuss-type proton transfer mechanism involving water molecule rotation. Neutron diffraction and *ab initio* molecular dynamics[4] further highlight the crucial role of hydrogen disorder and vacancies in optimizing proton transport. These insights pave the way for designing new multifunctional materials for energy conversion.

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Nb_6/Ta_6 Metal Atom Cluster Materials: Facile Large Quantity Preparation and New Materials

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Keywords : Hexanuclear Cluster Compounds, Synthesis, X-tray Structures, Reactivity

A prominent research area is that of hexanuclear cluster compounds of electron-poor transition metals with octahedral metal atom core.[1] A large number of halide supported octahedral cluster compounds are known of the metals niobium and tantalum, of which many are prepared by solution-chemical methods. Such methods allow for ligand exchange reactions, which give access to many different cluster compounds and allows for a delicate adjustment of the materials properties of such cluster compounds. In order to investigate materials properties a preparative procedure was developed, which quickly, fast and easy allows for the preparation of larger amounts of $[Nb_6Cl_{14}(H_2O)_4].4H_2O$. This compound is used for a long time as starting material for other Nb_6-cluster compounds.[2] Besides this procedure the preparation and single-crystal X-ray structures of some new Nb_6-cluster compounds with O-donor ligands, like $[(Nb_6Cl_{i12})Cl_{a2}(H_2O)_{a4}]\cdot 7$ Pyr (pyr = pyridine, Figure 1) is presented. Furthermore, some rarely observed Ta_6-clusters with only 13 cluster-based-electrons, supported by alkoxide-ligands (Figure 2), are presented.[3] The structure of one example, $(PPh_4)[Ta_6(OC_2H_5)_{12}I_6]\cdot C_2H_5OH$, is shown in Figure 2.

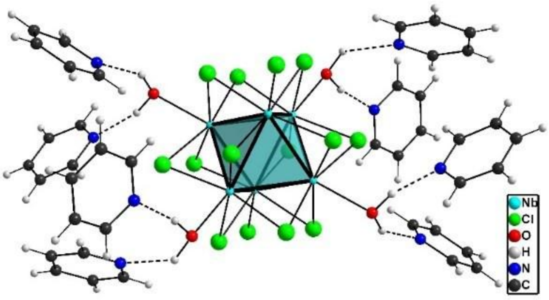

Figure 1. Structure of the neutral $[(Nb_6Cl^{i}_{12})Cl_{a2}(H_2O)^{a}_4]$ cluster surrounded by hydrogen bonded pyridine molecules.

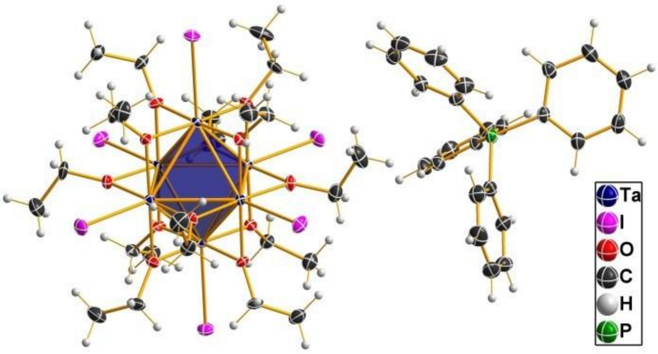

Figure 2. Structure of the ion pair in crystals of $(PPh_4)[Ta_6(OC_2H_5)_{12}I_6]\cdot C_2H_5OH$ with 13 CBE cluster ions.

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Record-high hyperpolarizabilities in atomically precise single metal-doped silver nanoclusters

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Recent developments in nonlinear optical (NLO) imaging techniques, notably multiphoton imaging and second harmonic generation imaging, have motivated intensive research in developing targets with high NLO response. Biological tissues exhibit optically transparency in the near-infrared (NIR) region, making NLO-phores capable of absorbing NIR light through nonlinear optical processes highly valued for bio-imaging [1]. For instance, ligand-protected gold nanoclusters have drawn extensive research interest in the past decade due to their excellent photoluminescence, and NLO properties [2].

In this work, using the control of single metal doping on silver nanoclusters (Ag25 protected by thiolate SR = 2,4-dimethylbenzenethiol (DMBT) ligand), we aim to explore the effects of metal doping on the (photo)stability and the nonlinear optical response of liganded nanoclusters. We study two-photon excited photoluminescence and the second harmonic response upon excitation in the NIR (780–950 nm) range [3]. Emphasis is placed on the effect of metal doping to boost the second-order nonlinear optical scattering properties (first hyperpolarizability, $\beta(2\omega)$) of Ag25 nanoclusters. In particular, $\beta(2\omega)$ values are one order higher than the one reported for Au25 nanoclusters and represent the largest values ever reported for ligand-protected nanoclusters. The trends observed in the hyperpolarizability values were further corroborated by quantum mechanical calculations evidencing resonance effects. Such enhanced hyperpolarizability leads to a strong second harmonic response and renders them attractive targets in bioimaging.

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Chirality's transfer's entangled relationship with shape

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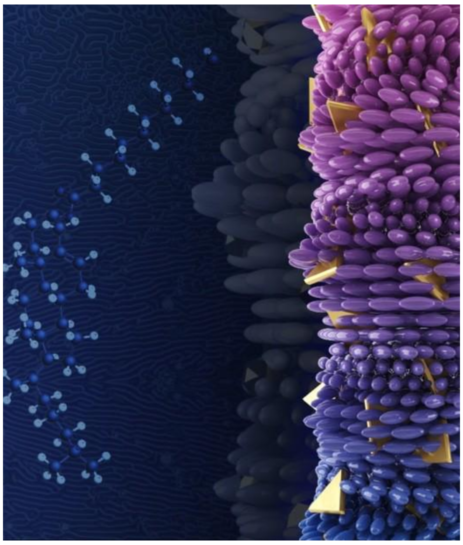
The focus of our work is to understand and then establish design rules for the amplification of chirality through space by nanoshapes either intrinsically chiral or capped with chiral organic ligand shells. We established that the induced chiral nematic liquid crystals (N*-LC) phases as a reporter medium in combination with calculations of a suitable pseudoscalar chirality index permit visualization and ranking of the extent of chirality transfer and amplification from chiral nanomaterials to a surrounding achiral N-LC medium. These studies examine size, shape, nature and type of surface functionalization of chiral nanomaterials. Our experiments revealed that more effective chirality transfer to a bulk N-LC occurs when a chiral monolayer-protected surface is broken up into small nanoparticle 'pieces'.[1] Here, the presence of chiral ligand-capped gold nanoparticles (GNP) results in helical distortions of a much larger number of N-LC host molecules surrounding each GNP when compared to their organic chiral molecular counterparts.[2] Hence, the chiral correlation length for the same chiral structure or molecule is significantly larger when it is confined at a certain density to a curved nanoscale interface and drastically larger when this curved nanoscale surface is desymmetrized as, for example, in gold nanorods[3,4] with higher chiral anisotropy (g) factors.



This approach is so sensitive that even miniscule changes in the molecular structure of the chiral molecules capping the gold nanorods can now be established and compared with respect to their molar helical twisting power (β_{mol}). We are now able to predict shape effects with respect to the efficacy of chirality transfer based on the product of such pseudoscalar chirality indicator $\left|G^{a}_{oa,max}\right|$ and a geometric shape compatibility factor S^{XN} based on the two-dimensional isoperimetric quotients for such nanoshapes in a nematic solvent.[5] These concepts were further extended to cellulose nanocrystals[6] with intrinsic chirality (molecular and morphological)[7] as well as the lyotropic chromonic nematic LC phase.[8] Finally, we are extending these concepts to discotic nematic (N_D) LC phases; experiments that further support our earlier arguments of maximum chirality transfer efficacy facilitated by shape complementarity. These studies now include intrinsically chiral gold nanoshapes such as nanotriskelions.[9]

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Sustainable circularly polarized emission from cluster-embedded bent-core liquid crystals systems for advanced optoelectronic applications

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Keywords: transition metal cluster, liquid crystal, bent core, chirality, luminescence, CPL

Circularly polarized luminescence (CPL) has attracted wide research interest over the past decade[1] due to its potential in advanced technologies such as optical information encryption and storage, anticounterfeiting tags, 3D displays, etc[2–4]. Research efforts have focused on the development of efficient chiral emitters exhibiting high luminescence dissymmetry factors (g_{lum}) and tunable emission properties. One promising strategy revolves around emissive liquid crystals (LC). In this work, we report the design of a CPL-active hybrid system based on a supramolecular self-assembly approach. The system integrates bent-core liquid crystal (BCLC), which organize into nanoscale or microscale layered B4 filament morphologies[5] (Figure 1a) with red phosphorescent transition metal clusters[6] as emitters (Figure 1b).

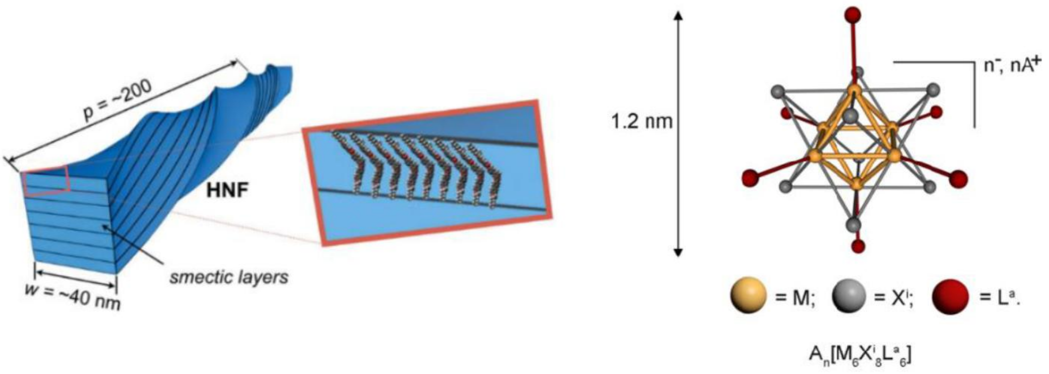

Figure 1: a) Helicoidal NanoFilament formed by Bent Core molecules b) Structure of an octahedral transition metal cluster

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Optical Properties of Gold Clusters Following Surface-Modification by Hydrogen Exposure

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The adsorption of hydrogen on small nanoparticles has garnered attention due to its potential applications in catalysis, energy storage, and hydrogen detection. The importance of the surface modifications and of resulting structural transformations under hydrogen exposure have been demonstrated experimentally and studied theoretically [1]. The consequences for the catalytic activity of gold nanoparticles are far-reaching, potentially explaining its size-dependence [1].

In the present work, we study the consequences of the surface modifications following hydrogen exposure on the optical properties. To calculate the optical response, we employ real-time TDDFT+*U* calculations which correct the description of the electronic d band. This has been shown for silver clusters to lead to excellent results [2]. We discuss, in particular, the distinction of chemical and structural effects of the surface modification.

Gold nanoparticles are a well-known efficient plasmonic system when clean and pure. In our present work, we show that the gold nanoparticles lose their strong surface-plasmon resonance upon hydrogen exposure. This effect might possibly be exploited for the realization of gold-cluster-based hydrogen detectors.

Furthermore, we identify surface-confined super-atom states in addition to the usual volume super-atom states. The change of the optical properties is, in particular, linked to the loss of super-atom character of the states above the gold d band.

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Shaping Light: Bent-Core Liquid Crystals and Clustomesogens for High-Performance Circularly Polarized Devices

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Understanding and controlling the polarization of light is a powerful strategy for enhancing optical performance, increasing resolution, and maximizing device efficiency. This research explores a unique class of liquid crystal (LC) materials with the potential to advance high-resolution optics and support sustainable energy practices through circularly polarized luminescence (CPL). LC-based structures typically exhibit dissymmetry factors — a measure of the differential emission of left- and right-handed CPL — that are an order of magnitude higher than those of conventional small organic molecules, helical macromolecules, or synthetic polymers.[1]

In this study, we harness the naturally twisted morphologies of bent-core liquid crystals (BCLCs) to design CPL-active systems adaptable to a wide range of applications.[2] Realizing the full potential of LC-CPL systems requires custom-tailored properties such as high quantum yield at specific wavelengths, tunability, and dynamic responsiveness. This presentation will show how BCLC helical templates can be used to host functionalized emitters, specifically, self-organized hybrid organic– inorganic nanomaterials known as clustomesogens. By integrating LC-based templates with LC-based emitters, we can achieve dynamic, self-assembled superstructures that allow external stimuli to manipulate the system's organization, leading to ultra-high dissymmetry factors and unprecedented control over CPL properties.[3]

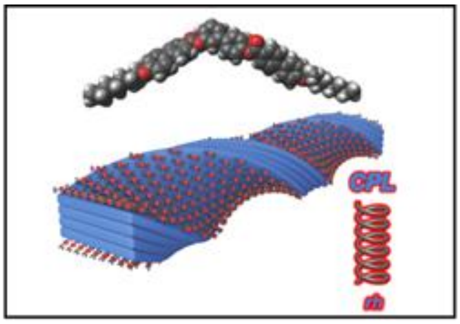

***Fig. 1:** Twist it, light it: all-in-one LC System*

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Living Libraries of Intermetallic Superatoms

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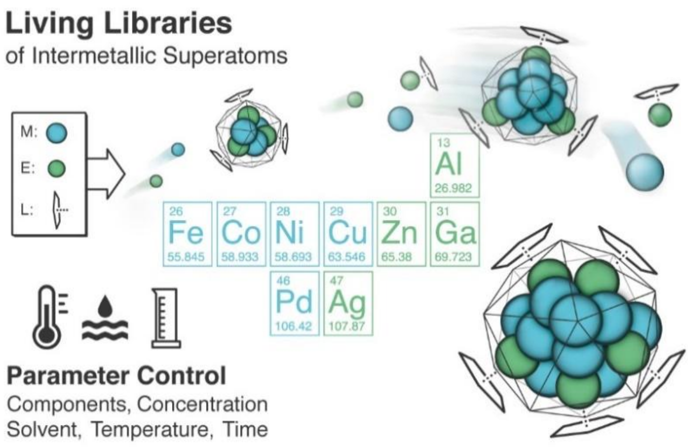
Keywords: Intermetallic Clusters, Superatoms, Catalysis

Intermetallics of metals of very different properties (M/E) can potentially substitute industrial catalysts based on rare and precious metals [1]. To realize this opportunity, atom-precise catalyst design is required at the size regime of ≤ 1 nm, where every metal atom counts. Such intermetallic clusters are molecular counterparts of the solid-state M/E materials [2]. Recently, we discovered a way to generate 'living libraries' of meta-stable, all-hydrocarbon ligated, intermetallic clusters $[M_aE_b](R)_n$ [3]. The living libraries of ligated mixed-metal clusters are generated by organometallic precursor chemistry. The term "living" refers to the population with interrelated clusters, including transient and highly reactive clusters, as well as more accessible but less reactive ones. The libraries are sensitive to perturbation. The evolution is monitored by high resolution liquid injection field desorption mass spectroscopy (LIFDI-MS).

To demonstrate proof of concept we generated a rich library of all-hydrocarbon ligated Cu/Zn clusters, "embryonic brass" and characterized it *via* LIFDI-MS using double labelling and varied collision energy experiments. A computational framework was developed by our collaboration partners, combining density functional theory (DFT) with a tight binding approach, suited to analyze the full compositional configuration space, that yields a set of structures for each cluster of the library [3]. Through this methodology it is possible to efficiently characterize the clusters' structure reactivity relationships without the need of isolation of specific clusters. This is highlighted by the formate containing species $[Cu_{11}Zn_6](Cp^*)_8(CO_2)_2(HCO_2)$ and by the alkyne semi-hydrogenation catalyst $[Cu_9Zn_7](Cp^*)_6(\eta^2\mu^1$-hexyne-3)$(\eta^2\mu^1$-hexene-3)$(\eta^1\mu^2$-hexenyl-3). The former species was detected after stepwise perturbation of the initial library with carbon dioxide and dihydrogen and the later species was identified after treatment with 3-hexyne and dihydrogen, starting out either from the initial library or from the previously isolated pre-catalyst cluster $[Cu_4Zn_{10}](Cp^*)_8$.



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Niobium Oxyiodide Cluster Compounds from Heterogeneous Solid-State Reactions by means of Non-Conventional Reduction

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Metal-rich niobium iodides involve the compounds Nb_6I_{11}, Nb_3I_8, NbI_3, and NbI_4. An interesting extension of the niobium halide chemistry is achieved by the employment of an additional non-metal element, leading to heteroanionic cluster compounds, as exemplified for Nb_6I_9S, Nb_3X_7S, Nb_3TeI_7, $Nb_4Se_4I_4$, $Nb_7S_2I_{19}$, Nb_4PnX_{11} with Pn = N, P, X = Cl, Br, I, and so on. The presence of a chalcogenide or pnictide anion has an impact on the cluster design, the connectivity of clusters, and on the electronic properties. For example, compounds ANb$_3$Br$_7$S with A = Rb, Cs have been referenced for their potential Luttinger liquid behaviour. [1]

The system Nb–O–I system, which compromises the already known compounds $NbOI_3$, NbO_2I, and $NbOI_2$, was recently a subject of our investigations with a focus on the development of niobium-rich compounds. The formation of metal-rich compounds in this system is highly sensitive to changes in conditions, such as temperature and composition, leading to the formation of different metal oxyiodide phases. Another important issue for the preparation of metal-rich compounds is the choice of an appropriate, preferably soft, reduction agent.

Actually, we have prepared novel niobium oxyiodide compounds by employing $Li_2(CN_2)$ as a non-conventional reduction agent. It can be shown, that the interplay between the reactants NbI_4, $Li_2(CN_2)$ and Li_2O is forming a heterogeneous system in a fused silica ampoule, at around 500 °C in which local temperatures and concentrations have an important impact on the phase formation. As a result, we have identified a number of niobium-rich cluster compounds, namely Nb_4OI_{12},[2] Nb_4OI_{11},[3] Nb_4OI_{10},[3] Nb_5OI_{11}, $Li_3[Nb_7O_5I_{15}]$, and $Nb_8O_5I_{17}$ that are all obtained from the same aforementioned reaction mixture. Their crystal structures, their modular construction scheme, their electronic properties, and their electrical conductivity properties are reported in this presentation.

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Polypnictogen Ligand Complexes As Building Blocks For Supramolecular Aggregations

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Keywords: Pnictogens, Supramolecular Chemistry

Polypnictogen ligand complexes of phosphorus and arsenic are activated forms of white phosphorus and yellow arsenic and therefore interesting starting materials for further transformations in terms of an atom-efficient way to organo-substituted pnictogen derivatives. Moreover, the isolobal tetrahedral complexes $[\{Cp^RMo(CO)_2\}_2(\mu,\eta^2\text{-}EE')]$ (E = P-Bi; E' = P-Sb) are valuable building blocks for self-assembling reactions[1]. Furthermore, the five-fold symmetric *cyclo*-P_5 ring of the pentaphosphaferrocenes $[Cp^RFe(\eta^5\text{-}P_5)]$ enables the use of these complexes in unique supramolecular aggregations with Lewis-acidic transition metal moieties to form unprecedented giant spherical molecules[2] (Figure 1). The talk will focus on latest results in the supramolecular chemistry of the Mo_2EE' tetrahedral compounds and pentaphosphaferrocenes and will present smaller[3] and larger supramolecular aggregates[4].

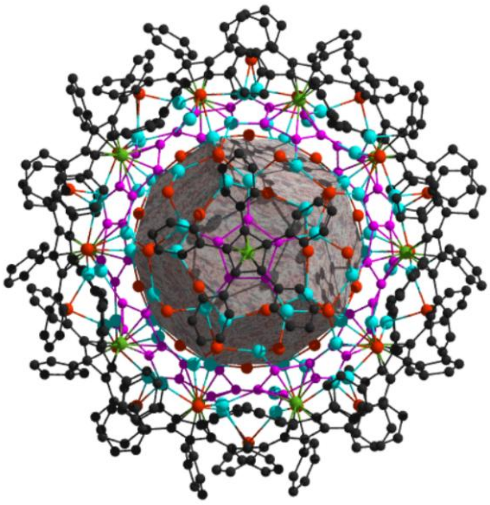

Figure 1. $[Cp^RFe(\eta^5\text{-}P_5)]$ as a building block for giant supramolecular spheres

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Supramolecular self-assembly of nanotubes based on inorganic nano-ions and organic macrocycles

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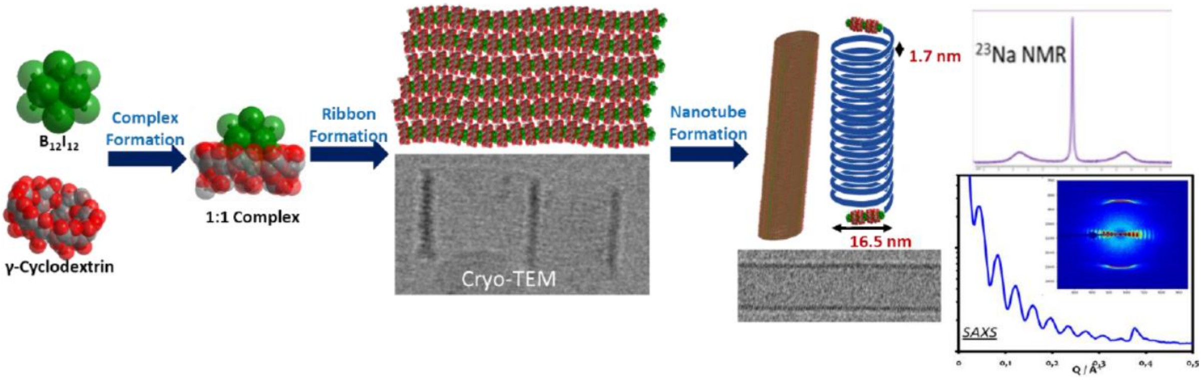
Nano-ions represents a broad class of inorganic compounds that include polyoxometalates, metal-atom clusters, or closo-borates. A key feature of these nano-ions is their low volumetric charge density, which imparts remarkable supramolecular properties in aqueous solutions. [1] These arise from a powerful solvent effect, namely the chaotropic effect, which gives them ability to self-assemble with non-ionic organic substances like cyclodextrins or surfactants, leading to host-guest complexes or hybrid vesicles. [2] Recent publication showed formation of discrete supramolecular host-guest complex between γ-cyclodextrin and the dodecaborate anions [B12X12]2- with X = Cl, Br or I. [3] Our reinvestigation revealed that these systems can undergo supramolecular polymerization, producing in fine either crystalline materials built from 1D-bamboo chains or water-soluble hybrid nanotubes.

In this communication, we present multi-scale characterizations of these systems, discussing both their structures and formation pathways. Solution studies were conducted using multinuclear NMR (1H, 11B, and 23Na), dynamic light scattering, and small- and wide-angle X-ray and neutron scattering. Direct observation of the nanotubes was achieved using cryogenic electron microscopy, which revealed highly monodisperse self-assembled nanotubes. This data set shows that the local structure of the hybrid nanotubes closely is reminiscent to that of the 1D bamboo chains, as determined by single-crystal X-ray diffraction.



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Exploring New Properties of Molybdenum Cluster Chalcogenides via First-Principles Calculations

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Since their discovery in the earliest 70's, Chevrel phases (MxMo6X8; M = Ag, Sn, Ca, Sr, Ba, Sn, Pb, 3d elements or lanthanides; X = S, Se, or Te; $x = 0-4$) [1] have been extensively studied, mainly for their superconducting properties [2], but also for other various applications in magnetic devices, catalysis [3], batteries [4], or thermoelectricity [5]. Concerning catalytis, Chevrel phases demonstrate high performance for many fundamental catalytic reactions such as hydrogen evolution [6], oxygen reduction [7], nitrate conversion to ammonia [8], and CO2 reduction reaction [9] to mention a few. This is due to the unique combination of their peculiar electronic structure, low-coordinate molybdenum atoms, tuneable oxidation state, thermal stability, and dual Lewis acidity and basicity [3]. We started to investigate how these interesting electronic properties can affect different catalytic mechanisms to achieve high catalytic activity. Some preliminary results obtained in the case of CO2 reduction reaction will be presented.

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Thermoelectric Molybdenum Sulfides: A Theoretical Study

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Reduced molybdenum chalcogenides with a framework built up by Mo clusters have attracted significant interest since the discovery of the Chevrel phases and related cluster compounds [1]. Several have been the subject of investigations to assess their thermoelectric performance in a broad range of temperatures. Some of them show very low, glass-like lattice thermal conductivity [2].

Recently, the synthesis of the new pseudo-romanechite compound Tl0.58Mo3S5, in both monocrystalline and polycrystalline forms, has been reported [3]. This compound is closely bonded to Mo2S3: Both crystal structures exhibit infinite zigzag Mo chains. Their crystal structures give rise to the formation of tunnels measuring [1 × 2] and [2 × 3] octahedra for Mo2S3 and Tl0.58Mo3S5, respectively. These tunnels are empty in Mo2S3 whereas they are occupied by Tl in Tl0.58Mo3S5. Another common feature of these two compounds is the presence of modulations in their crystal structure.

Thermoelectric power measurements showed that the primary charge carriers in Mo2S3 are holes [4]. Recent measurements of low-temperature transport properties suggest that Tl0.58Mo3S5 behaves like a narrow bandgap n-type semiconductor [3]. This behavior distinguishes this compound from molybdenum cluster chalcogenides, all of which exhibit p-type behavior at high temperatures [2].

To better understand their transport properties, we have studied Mo2S3 and Tl0.58Mo3S5 using periodic DFT calculations. A special attention has been paid to electronic structure of the infinite chain, and their potential distortions due to the modulations, as well as the influence of interactions between the chains. The influence of the structural properties on the electronic transport properties has been analyzed using semi-classical transport simulations based on band structure calculations.

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Poster

PO1

$Ag_{108}(PEt_3)_{24}Cl_6$: A hexagonal prismatic metalloid cluster and beyond

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Keywords: Silver, metalloid cluster, cluster growth

While the gold cluster chemistry has been a focus of interest for decades, the advent of metalloid silver cluster research only began with the characterization of $[Ag_{44}(p\text{-MBA})]^{4-}$ by Bigioni and co-workers in 2013. [1] Today, large clusters with up to 374 silver atoms can be readily prepared. [2] Still, most stable metalloid silver clusters rely on thiolates for stabilization. In search for thiolate-free stable clusters, our group synthesized the compound $Ag_{64}(PBu_3)_{16}Cl_6$ by reduction of the precursor Bu_3PAgCl with L-Selectride. [3] Using a different phosphine as the ligand, the remarkably light and temperature sensitive metalloid cluster $Ag_{108}(PEt_3)_{24}Cl_6$ can be obtained with high yields. [4] While most examples feature a spherical shape and fcc packing within their core, this compound features a distinct hexagonal prismatic shape and an hcp-layered kernel. Due to structural relationships both to Ag_{64} as well as to another series of related silver clusters, $Ag_{108}(PEt_3)_{24}Cl_6$ might prove to be an ideal candidate to understand cluster growth. Furthermore, it might be used as a model compound for hexagonal prismatic nano plates, giving insights that cannot be obtained for those larger, not atom precise materials.

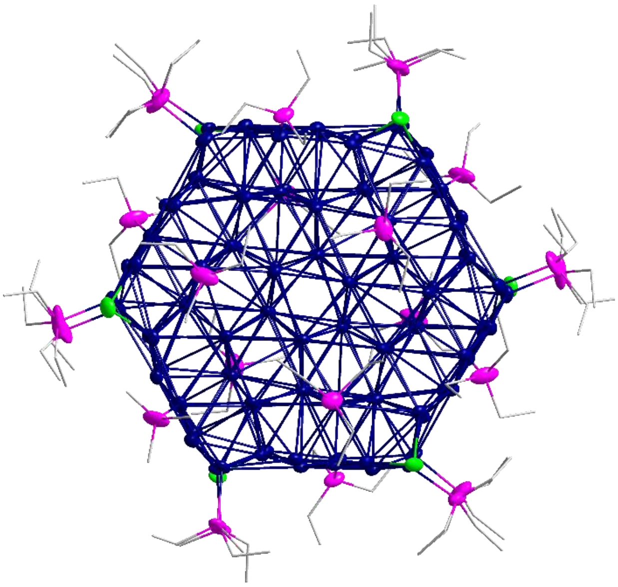

Figure 1: Molecular structure of $Ag_{108}(PEt_3)_{24}Cl_6$. Ag (blue), P (pink), Cl (green); Thermal ellipsoids set at 50% probability. C (grey) are shown as wireframe model. H atoms are omitted for clarity.

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PO2

$Ag_{12}\{Ge_9Hyp_2\}_6$: An Intermetalloid Cluster with bis-Silylated Ge_9-Units

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Keywords: Intermetalloid cluster, germanium, silver

The reaction of silylated Ge_9 clusters with coinage metal halides results in the formation of complexes in which one or two stabilised coinage metal atoms are coordinated to the Ge_9-cluster core. [1][2] We now report the synthesis and characterization of the novel intermetalloid cluster compound $Ag_{12}[Ge_9(Hyp)_2]_6$, exhibiting a silver core with coordinated bis-silylated Ge_9-clusters.

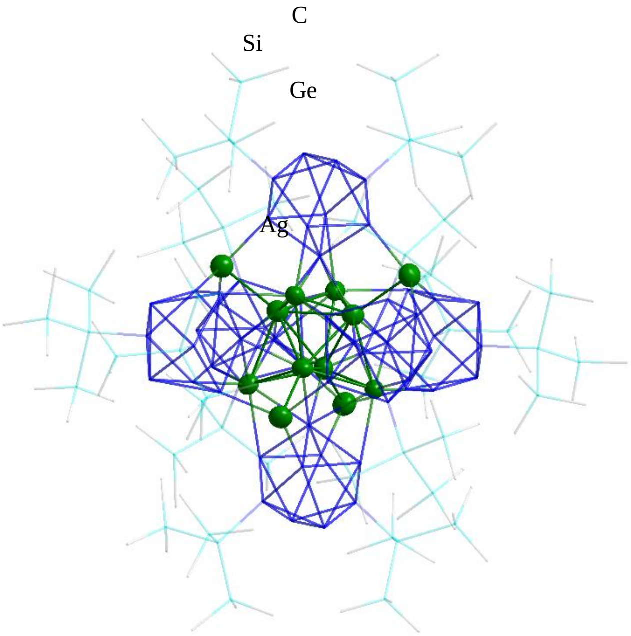

Figure 1: Molecular structure of $Ag_{12}[Ge_9(Hyp)_2]_6$ without hydrogen atoms. The $[Ge_9\ (Hyp_2)]$-Units are shown as wire and stick model.

The new intermetalloid cluster has an Ag_{12} metal cluster core to which six $[Ge_9(Hyp)_2]$ units are coordinated, acting as ligands. The $[Ge_9(Hyp)_2]$ units are arranged octahedrally around the Ag_{12} core, leading to a variety of Ag-Ge bonds and contacts. The cluster is a first example of an intermetalloid cluster, exhibiting a silver core, shielded by $[Ge_9(Hyp)_2]$ units.

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PO3

Exploring the Synergistic Electrochemical Benefits of a Niobium-Doped MoO3/Ta2O5 Catalyst for an Enhanced Oxygen Evolution Reaction

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Keywords: Niobium; Doping; MoO3/Ta2O5; Electrocatalysis; OER.

This study delves into the synergistic electrochemical advantages of a niobium-doped molybdenum trioxide (MoO3) nanorods combined with a tantalum pentoxide (Ta2O5) catalyst to increase the efficiency of the oxygen evolution reaction (OER). In light of the increasing demand for sustainable energy solutions, the imperative to develop efficient electrocatalysts conducive to water splitting, a critical process in hydrogen production, becomes evident. This investigation involves the synthesis of a niobium-doped MoO3/Ta2O5 composite and comprehensively evaluating its structural, electrochemical, and catalytic properties through various spectroscopic and electrochemical techniques. These findings highlight that incorporating niobium markedly enhances the electronic conductivity and availability of active sites within the catalyst, resulting in improved OER performance. Comparative analyses against conventional electrocatalysts underscore that the 8% niobium-doped MoO3/Ta2O5 composite demonstrates lower overpotentials (238 mV/cm2) and higher current densities, indicating its significant potential for practical applications. Furthermore, the robust metal-support interactions enabled by the Ta2O5 support stabilize the active phase and increase the catalyst's overall durability. This work yields valuable insights into the mechanisms of OER catalysis involving niobium-doped metal oxides, thereby underscoring the potential of such innovative catalyst designs in advancing hydrogen production technologies.

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PO4

$Ge_{14}Br_8(PPr_3)_4$ synthesis and applications

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Keywords: Germanium, metalloid cluster, cluster compound, disproportionation

Typical oxidation states of germanium are +II and +IV. Unusual subvalent binary germanium compounds Ge(I)X (X = Cl, Br) can be synthesised by the preparative co-condensation technique. [1] This method is a continuation of the matrix isolation technique and provides a unique starting material for the synthesis of metal-rich metalloid germanium clusters. In 2015, Schnepf and co-workers published the metalloid cluster Ge14Br8(PEt3)4 (1), which is the first subhalide germanium cluster with an average oxidation state of the germanium atoms lower than one. [2] Since 1 is insoluble in any common solvent, a better soluble cluster is required for subsequent investigations. For the synthesis of 1 PEt3 was used as the donor molecule.
Here we present a similar synthesis using PPr3 as the donor molecule during the co-condensation reaction to give the much better soluble metalloid cluster Ge14Br8(PPr3)4 (2), obtained as an intermediate in the disproportionation reaction of Ge(I)Br.

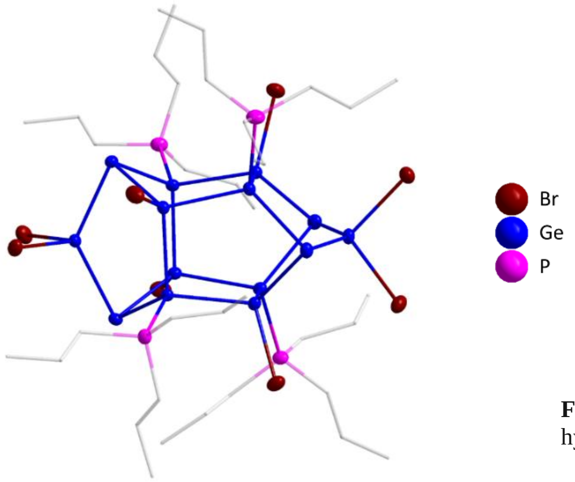

Figure 1: Molecular structure of Ge14Br8(PPr3)4 (2) without hydrogen atoms. The propyl groups are shown as a wire model.

2 is soluble in tetrahydrofuran and toluene, allowing NMR investigations. Variable temperature NMR investigations of the metastable subhalide Ge(I)Br solution provides insight into the formation of 2. In addition, the behaviour of 2 under laser irradiation is studied to check the applicability of 2 as a potential 'germanium ink' for direct laser induced writing, like gold printing. [3]

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PO5

Mechanically responsive luminescent nanocomposites

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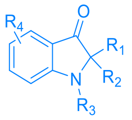
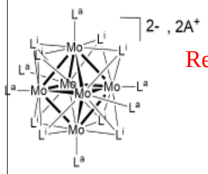
Responsive or smart materials are a class of materials that display properties modifiable upon various environmental changes like light irradiation, magnetic field, atmospheric composition or mechanical stress. As an example, mechanoresponsive luminescent (MRL) materials are able to translate directly mechanical inputs into detectable and processable optical signals and offer exciting possibilities of applications in the field of mechanical stress sensing.1,2 For instance, MRL materials can allow direct visualization of local curvatures or detection of damages ahead of structure failure with direct applications in clinical diagnosticor for the design of flexible and wearable devices or even security inks.3 However, this type of smart materials has not been commercially exploited for now because of the poor sensitivity and high cost/sensitivity ratio of explored systems (mostly polymers incorporating MRL organic compounds4).

We present here a radically new concept for mechanical stress detection with potential large-scale application, bypassing all prementioned issues. It relies on fast and reversible photophysical processes involving a tandem of non-mechanophoric emitters (an octahedral Molybdenum cluster compound (Mo_6) delivering a red NIR phosphorescence and a 3-oxindole organic derivative (Oxi) leading to a blue-green fluorescence signal, cf. *Figure 1*), whose emission efficiency depends on the O2 concentration in their surroundings. For some polymer families like the one chosen in our work, namely poly(urethane), O2 diffusivity and permeability are strongly affected by structural modifications induced by a strain.5 These changes in the local O2 concentration within the stressed film induce fast and reversible colour changes observable with naked eye when the functionalized polymers are subjected to mechanical stress *(Figures 2)*. The objective of the project is therefore to target the optimal hybrid copolymer composition to modulate strongly its internal O2 concentration when a UV-2A irradiation and a mechanical strain are applied, relying on photophysical and mechanical properties.



Blue-green emitter: 3-oxindole (Oxi)
R_1, R_2, R_3: alkyl chain, functional group, cationic organic moieties
R_4 : electron donating entity



Red-NIR emitter: Mo_6 cluster compound (Mo_6)
A^+: alkali cation, functional organic cation
L^i : halogen
L^a : halogen $-OCOC_nF_{2n+1}$

Figure 1: Representation of Oxi and Mo_6 emitters

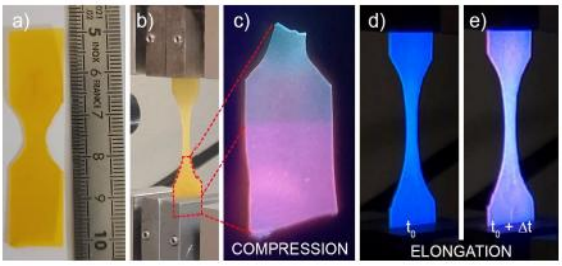


Figure 2: PU sample under normal light (a, b) and under UV-A irradiation (c, d, e)

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PO6

Octahedral Molybdenum Clusters and Graphene Oxide Nanocomposite Thin Films for Antibacterial Photoinactivation

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In the current context of microbial resistance to commonly used treatments, it is imperative to find alternatives to combat infections. A promising approach is to use antimicrobial coatings containing molecules capable of inactivating the proliferation of microorganisms through the application of visible light (photodynamic inactivation or PDI).

This thesis' works, supported by the Rennes University, are performed under the frame of the EIG Concert Japan PHOTOMOS-H_2O with our partners: IIC in the Czech Republic, the Waseda University in Japan, the University of Orleans and CNRS in France.

The main aim of this work is to design and study innovative hybrid coating films capable of efficiently inhibiting bacterial growth. To achieve this, we primarily focus on the integration of light-induced singlet oxygen generators: octahedral molybdenum cluster complexes with the formula $[Mo_6I_8X_6]^{2-}$ (Mo_6) on graphene oxide (GO) [1, 2].

The GO is synthesised using a modified Hummers' method [3]. To obtain thin layers integrating these two elements, several implementation techniques are being explored. Electrochemical deposition (ECD), electrophoretic deposition (EPD), dip coating, and spray techniques are promising for obtaining antibacterial coatings effective against a wide range of bacteria (Gram-negative and Gram-positive) and biofilms.

The hybrid films are characterised by various techniques such as XRD, SEM, EDS, XPS, Raman spectroscopy, and, most importantly, photoluminescence measurements showing whether nanocomposites are capable of producing reactive oxygen species (ROS), as singlet oxygen O_2 ($^1\Delta_g$), responsible for the inhibition of bacterial growth.

This study highlights the potential of hybrid coatings based on Mo6 and GO to combat bacterial infections, offering a promising alternative in the face of increasing antibiotic resistance.

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PO7

Photoluminescence and Photoelectrochemistry of Lead dinitrocarbonates

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Two lead-based compounds, $Pb_7I_6(CN_2)_4$ and $Pb_8O_4I_6(CN_2)$, were synthesized via solid-state and ceramic methods, respectively, and structurally characterized by single-crystal X-ray diffraction. $Pb_7I_6(CN_2)_4$ crystallizes in the hexagonal space group $P6_3/mmc$ and features a three-dimensional network of Pb tetrahedra, trigonal bipyramids, and octahedra interconnected by iodide and carbodiimide ($[NCN]^{2-}$) anions. $Pb_8O_4I_6(CN_2)$, obtained from PbI_2, PbO, and $Pb(CN_2)$, adopts a monoclinic structure (*C2/c*) and exhibits a unique heterocubane-type $[Pb_4O_4]$ motif that forms dimers through iodine bridges, also linked via $[NCN]^{2-}$ units. Optical characterizations using diffuse reflectance UV-Vis spectroscopy, Tauc plot analysis, Mott-Schottky measurements, and low-temperature photoluminescence reveal both materials to be semiconducting. The structural diversity and optical properties highlight their potential in photocatalytic and optical applications.

PO8

Structural and Optical Modulation of Pt_1Ag_{18} Nanoclusters via Ligand Engineering: Tailoring One/Two-Photon Excited Photoluminescence

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Metal nanoclusters typically consist of a few to hundreds of metal atoms and are protected by surface ligands, exhibiting novel molecular-like optical properties. It has already reported that the surface ligands play a major role in enhancing the photoluminescne of gold nanoclusters through charge transfer from surface ligand to the gold core. Ligand engineering, e.g. ligand motifs and ligand shell rigidity are an interesting strategy to enhance emission efficiencies (both upon one- and two-photon excitation). In this work, based on one-pot synthesized [Pt1Ag18(AdmS)2(DPPP)6Cl6]2+ (where AdmSH is 1-adamantanethiol and DPPP is 1,3-bis(diphenylphosphino)propane), we aim at modulating its red emitting properties, by replacing the bulky AdmSH ligand with electron donating capability offered by the 2-fluorothiophenol ((C6H4F)S) ligand. The number of (C6H4F)S was adjusted and we produced two new ligand-protected Pt1Ag18 nanocluster, [Pt1Ag18(DPPP)6((C6H4F)S)xCl8-x]2+ (x = 0–6), and another with more thiol substitutions, [Pt1Ag18(DPPP)6((C6H4F)S)yCl8-y]2+ (y = 2–8). Nonlinear optical properties are investigated on these 3 nanoclusters, including two-photon excited photoluminescence, two-photon absorption and hyper-Rayleigh scattering, in the wavelength range of 700-1000 nm of femtosecond laser excitation. Particularly, the two-photon excited photoluminescence is strongly affected by resonance effects and by ligand engineering process. Higher ratio of fluorinated ligand can lead to much higher one-photon quantum yield and two-photon excited cross section. Then, we explore the concept of ligand shell rigidity by using bulky counterions to enhance both one/two photon photoluminescence. With our work, we demonstrate a ligand engineering strategy for optical modulation on nanoclusters, as well as provide attractive targets for multiphoton bioimaging.

PO9

Structural Modifications of $M_5O_4I_{11}$ (M = Nb, Ta) Cluster Networks from Heterogeneous Solid-State Reactions

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The cluster compounds *M*5O4I11 (*M* = Nb, Ta) and Ta5O4I11(TaI5) were obtained from heterogenious solid-state reactions and structurally characterized by single-crystal X-ray diffraction. Their crystal structures are based on the novel [*M*5O4] cluster core with metal (*M*) atoms arranged following the motif of a square pyramid. Iodide ligands contribute to different connectivities in the structures, resulting in (van der Waals type) waved layer structures. Two structural modifications exist for Ta5O4I11, denoted as a-Ta5O4I11 and b-Ta5O4I11, and the compound Ta5O4I11(TaI5) encloses [TaI5] molecules within voids of the structure. The two-dimensional nature of the structures and the presence of metal-to-metal bonding warrant investigation into electronic properties. This has been explored through optical band-gap measurements, electronic conductivity studies, electronic band structure calculations, and X-ray photoelectron spectroscopy.

PO10

Synthesis of Niobium Oxyiodide-Clusters through unconventional reduction

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The reduction of niobium tetraiodide (NbI4) in the presence of an oxygen source using lithium cyanamide (Li2CN2) has led to the formation of a series of niobium oxyiodide clusters. These reduction reactions yield previously unreported cluster architectures, resulting in unique structural motifs. A significant amount of these clusters crystallizes from the gas phase as the system is gradually cooled to ambient temperature. The nature and composition of the resulting products are strongly influenced by the applied temperature profile and thermal gradient, highlighting the critical role of reaction conditions in directing the formation of the new cluster compounds.

PO11

$Ti_3C_2T_x$ Nanosheet/$NiFe_2O_4$ Nanoparticle Composites for Electrocatalytic Water Splitting

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This study reports the synthesis and detailed characterization of a Ti3C2Tx sheets/NiFe2O4 ferrite nanocomposite designed to enhance bifunctional electrocatalytic water splitting. Utilizing a facile hydrothermal approach, the nanocomposite effectively combines the exceptional electrical conductivity and high surface area of MXene sheets with the outstanding catalytic properties of NiFe2O4 ferrite nanoparticles. Comprehensive characterization through X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) confirmed the successful integration of NiFe2O4 nanoparticles onto the MXene nanosheets. Furthermore, X-ray photoelectron spectroscopy (XPS) revealed significant electronic interactions between the MXene substrate and NiFe2O4 ferrite nanoparticles, which are critical to the observed enhancement in catalytic performance. Electrochemical evaluations demonstrated that the synthesized Ti3C2Tx/NiFe2O4@20% (MNFO20) nanocomposite exhibits remarkable bifunctional catalytic activity, achieving an overpotential of 181 mV for the oxygen evolution reaction (OER) and 157 mV for the hydrogen evolution reaction (HER) at a current density of 10 mA cm–2 in both alkaline and acidic environments. Notably, the nanocomposite exhibited excellent stability, retaining its catalytic performance after 3000 cycles. The synergistic interaction between the MXene nanosheet and NiFe2O4 ferrite nanoparticle leads to optimized adsorption energies for the reaction intermediates, thereby enhancing overall catalytic efficiency. This work introduces a strategy for developing high-performance and cost-effective electrocatalysts for water-splitting applications, contributing to advancements in renewable energy technologies.

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