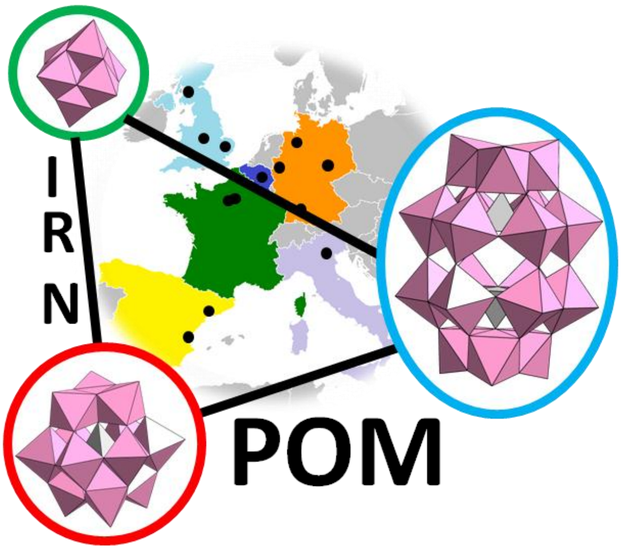
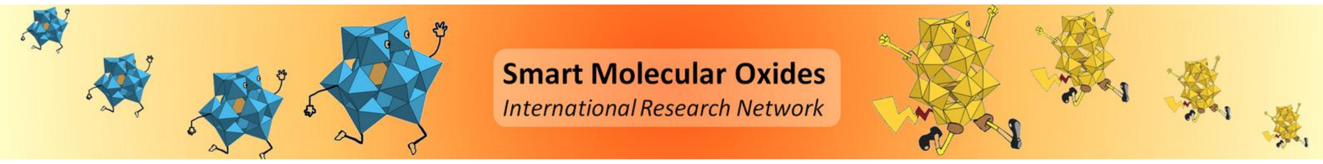
BOOK OF ABSTRACTS



SMART MOLECULAR OXIDES
INTERNATIONAL RESEARCH NETWORK

Symposium in Paris; September 2nd-3rd 2021



Symposium in Paris September 2-3 2021

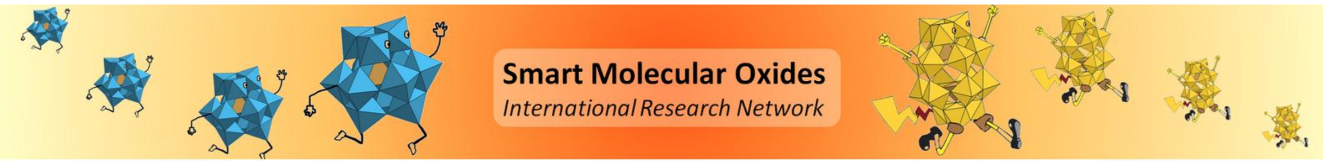
SCHEDULE

Thursday 2nd of Sept.

8h30	1h		Registration - Opening
9h30	45'	L1	May NYMAN (Oregon State University)
10h15	15'	C1	Natalya IZAROVA (RWTH Aachen University)
10h30	1h		Coffee Break + Poster
11h30	25'	K1	Carles BO (ICIQ)
11h55	15'	C2	Magda PASCUAL-BORRAS (Newcastle University)
12h10	25'	K2	Saurav BHATTACHARYA (Jacobs University)
12h35	1h30'		Lunch
14h05	25'	K3	Laurent RUHLMANN (Univ. de Strasbourg)
14h30	15'	C3	Albert SOLE-DAURA (Collège de France)
14h45	25'	K4	Juan Ramon GALAN-MASCAROS (ICIQ)
15h10	15'	C4	Ludivine K/BIDI (Sorbonne Université)
15h25	15'	C5	David SALAZAR MARCANO (KU Leuven)
15h40	1h20		Coffee Break + Poster
17h00	25'	K5	Clément FALAISE (Institut Lavoisier de Versailles)
17h25	15'	C6	Scott FOLKMAN (ICIQ)
17h40	15'	C7	Kevin MALL HAIDARALY (Sorbonne Université)
17h55	15'	C8	Roger SANCHIS-GUAL (Valencia University)
18h10	25'	K6	Lee CRONIN (University of Glasgow)
18h35			Free time
19h30			Dinner 19h45-21h15

Friday 3rd of Sept.

9h00	25'	K7	John ERRINGTON (Newcastle University)
9h25	15'	C9	Nicolas MARTIN (Oregon State University)
9h40	25'	K8	Xavier LOPEZ (Universitat Rovira i Virgili)
10h05	1h		Coffee Break + Poster
11h05	15'	C10	Laia,VILA-NADAL (University of Glasgow)
11h20	15'	C11	Antoine BONNEFONT (Université de Strasbourg)
11h35	25'	K9	Mauro CARRARO (University of Padova)
12h00	15'	C12	Nada SAVIC (KU Leuven)
12h15	2h		Lunch
14h15	15'	C13	Anne VALLEE (Institut Lavoisier de Versailles)
14h30	15'	C14	Francisco DE AZAMBUJA (KU Leuven)
14h45	15'	C15	Cécile HUEZ (Sorbonne Université, IEMN)
15h00	15'	C16	Eduard GARRIDO RIBO (University of Glasgow)
15h15	25'	K10	Eugenio CORONADO (Valencia University)
15h40	10'		Closing session
15h50			Coffee break



THURSDAY 2ND OF SEPTEMBER

8h30 Registration - Opening
Anna PROUST, *Sorbonne Université*, *France*
Emmanuel CADOT, *Université de Versailles-St-Quentin-en-Yvelines*, *France*

9h30 Group IV Metal Oxo Clusters and Materials(L1)
May NYMAN, *Oregon State University, USA*

10h15 Unusual Reactivity via Polyoxotungstate Functionalization (C1)
Natalya IZAROVA, *RWTH Aachen University, Germany*

10h30 Coffee break + Poster

11h30 How IPAs are made? The answer to Mo, W, V, Nb and Ta IsoPolyAnions from the POMSimulator (K1)
Carles BO, *Institute of Chemical Research of Catalonia*, *France*

11h55 Electron-Rich Polyoxometalates for Energy Storage Applications (C2)
Magda PASCUAL-BORRAS, *Newcastle University*, *UK*

12h10 Charge Modulation In Pd-Based Oxo-Clusters And Their Use In Heterogeneous Catalysis (K2)
Saurav BHATTACHARYA, *Jacobs University*, *Germany France*

12h35 Lunch

14h05 Hybrid (iso)porphyrin – polyoxometalate Materials (K3)
Laurent RUHLMANN, *Université de Strasbourg, France*

14h30 Computational Investigation On The Role Of POMs In The CO_2 Photoreduction Catalyzed By (POM,Cat)@MOF/POP Composites (C3)
Albert SOLE-DAURA, *Collège de France*, *France*

14h45 Heterogeneous Electrocatalytic water oxidation with polyoxometalates (K4)
José Ramón GALAN-MASCAROS, *Institute of Chemical Research of Catalonia*, *France*

15h10 Storage Of Electrons And Protons On Metalla-Silox Polyoxometalates (C4)
Ludivine B/BIDI, *Sorbonne Université*, *France*

15h25 Development of Novel Supramolecular Assemblies Based on Proteins and Polyoxometalates (C5)
David.E. SALAZAR MARCANO, *KU Leuven*, *Belgium*

15h40 Coffee break + Poster

17h00 Chaotropic Effect as Motif Assembly in POM Chemistry (K5)
Clément FALAISE, *Université de Versailles-St-Quentin-en-Yvelines*, *France*

17h25 Electrocatalytic Water Oxidation Beginning with POMs: Distinguishing Between Homogeneous and Heterogeneous Catalysis (C6)
Scott J. FOLKMAN, *Institute of Chemical Research of Catalonia, Spain*

17h40 Mesomorph polyoxometalate-based hybrids materials for photonics (C7)
Kevin MALL HAIDARALY, *Sorbonne Université*, *France*

17h55 Improving The Electrocatalytic Activity And Stability Of Prussian Blue Analogues By Introducing Au NPs (C8)
Roger SANCHIS-GUAL, *Instituto de Ciencia Molecular, Spain*

18h10 Digital Discovery of Molecular Metal Oxides and Chemputation (K6)
L. CRONIN, *University of Glasgow*, *UK*

18h35 Free time

19h30 Dinner (19h45 – 21h15)

FRIDAY 3RD OF SEPTEMBER

9h00 **Evolution of {MW_5} Lindqvist POM Synthesis (K7)**
John ERRINGTON, *Newcastle University*, *UK*

9h25 **The Decaniobate As Precursor For Polyoxoniobates (C9)**
Nicolas MARTIN, *Oregon State University, USA*

9h40 **Computational Study of the Staircase Molecular Conductivity of Polyoxovanadates Adsorbed on Au(111) (K8)**
Xavier LOPEZ, *Universitat Rovira i Virgili, Spain*

10h05 **Coffee break + Poster**

11h05 **Computational chemistry and molecular metal oxides (C10)**
Laia VILA NADAL, *University of Glasgow*, *UK*

11h20 **Mechanism of Nitrite reduction Electrocatalyzed by polyoxometalates (C11)**
Antoine BONNEFONT, *Université de Strasbourg, France*

11h35 **Polyoxomolybdates-peptides conjugates for cancer cell targeting (K9)**
Mauro CARRARO, *University of Padova*, *Italy*

12h00 **Hydrolysis of Insoluble Proteins by Zr-Substituted Polyoxometalates (C12)**
Nada D. Savić, *KU Leuven, Belgium*

12h15 **Lunch**

14h15 **New Generation of Hybrid Bisphosphonate Polyoxometalate Gold Nanoparticles for Biomedical Applications (C13)**
Anne VALLEE, *Université de Versailles-St-Quentin-en-Yvelines*, *France*

14h30 **Polyoxometalates as Inorganic Ligands for the Lewis Acid Catalyzed Direct Amide Bond Formation (C14)**
Francisco DE AZAMBUJA, *KU Leuven, Belgium*

14h45 **Redox State-Modulated Electron Transport Properties of Polyoxometalates at the Nanoscale (C15)**
Cécile HUEZ, *Université de Lille - Sorbonne Université*, *France*

15h00 **Molybdenum Reds: Highly Reduced Molybdenum Polyoxometalates Providing Unique Topologies Through *d*- And *f*-Block Ion Incorporation (C16)**
Eduard GARRIDO RIBO, *University of Glasgow*, *UK*

15h15 **Smart Magnetic POMs for Quantum Computing (K10)**
Eugenio CORONADO, *Instituto de Ciencia Molecular, Spain*

15h40 **Clossing session**

15h50 **Coffee break**

POSTERS

P-1 **New perspectives with lindqvist-type hybrid POMs in host-guest supramolecular chemistry**
Ibrahima Fa BAMBA, *Université de Versailles-St-Quentin-en-Yvelines*, *France*

P-2 **Modular Design of Noble Metal-free Mixed Metal Oxide Electrocatalysts for Complete Water Splitting**
Dandan GAO, *Ulm University, Germany*

P-3 **Supramolecular hybrid networks based on polyoxometalates and cyclodextrins**
Maxence LION, *Université de Versailles-St-Quentin-en-Yvelines*, *France*

P-4 **Polyoxometalate/Silica-Templated 2D Mesoporous N-P-Carbon Supported Ni clusters/MoC/MoO$_2$ for Water Oxidation**
Rongji LIU, *Ulm University, Germany*

P-5 ***Title***
Juba SALHI, *Sorbonne Université*, *France*

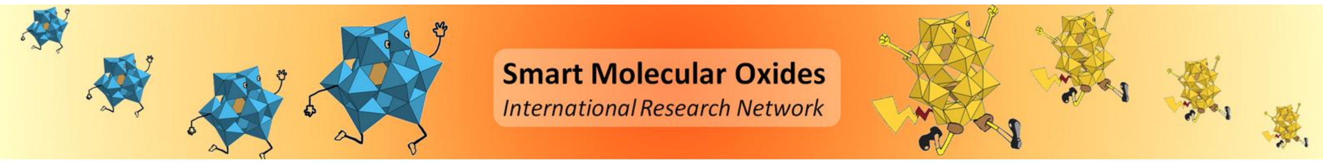
P-6 **Synthesis of Novel MW$_5$ Lindqvist-type Polyoxometalates**
Dominic SHIELS, *Newcastle University*, *UK*

P-7 **Synthesis and Supramolecular Studies of an Elusive Polyoxopalladate Nano-Wheel in Aqueous Solution**
Zoe SINCLAIR, *University of Glasgow*, *UK*

P-8 **Polyoxometalate-Supported Bioinspired Catalysts for Small Molecules Activation**
Weixian WANG, *Sorbonne Université*, *France*

P-9 **Ground-State Charge Transfer in Vanadium-Containing Polyoxometalates With Phthalocyaninato Lanthanide Ions**
Irina WERNER, *Leibniz Institute of Surface*, *Germany*

P-10 **Keggin-Type Ions in the Hofmeister Series**
Sa YAO, *Université de Versailles-St-Quentin-en-Yvelines*, *France*



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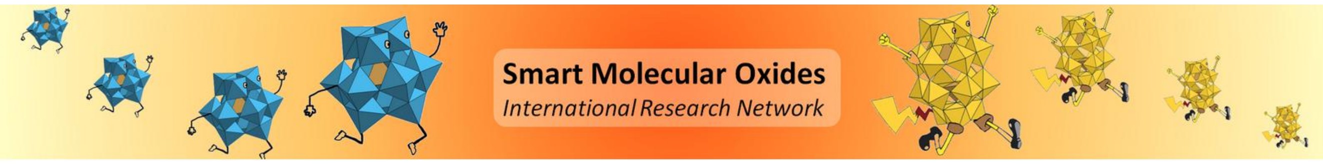
Lecture



GROUP IV METAL OXO CLUSTERS AND MATERIALS

May Nyman, Ian Colliard, Lauren Palys, Jim Sommers, Nicolas Martin, etc.
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Metal-oxo clusters are modular building blocks for materials. In water and organic solvents, balancing hydrolysis reactions and coordination chemistry is the key to new chemistries. Understanding and controlling solution phase reaction pathways from monomers to clusters to materials (and vice versa) will lead to new discoveries from across the periodic table, and most aspirational, the next new class of cluster-based materials. I will present an overview of our studies of the importance of the hard tetravalent metal cations ($\mathrm{Zr^{IV}}$, $\mathrm{Hf^{IV}}$, $\mathrm{Ce^{IV}}$, $\mathrm{Th^{IV}}$, $\mathrm{U^{IV}}$, $\mathrm{Np^{IV}}$, $\mathrm{Pu^{IV}}$) in materials science and actinide chemistry.

$\mathrm{Zr/Hf^{IV}}$ are popularly employed in metal-organic frameworks, acid catalysis reactions, and microelectronics. Less well-known but the most extensive use is in the nuclear industry, exploiting the neutron transparency of Zr and high neutron capture cross section of Hf. The very different nuclear chemistry renders efficient separation crucial, and the very similar chemistry challenges this endeavor. While the solid-state structural chemistry of Zr and Hf is deemed very similar, we show distinct differences in their cluster chemistry with peroxide, and with thiocyanate. The latter replicates the industrial process of their separation. Small-angle X-ray diffraction and crystallography studies differentiate hydrolysis/ligand coordination between Hf-SCN and Zr-SCN clusters as the driving force for separation of the two most similar metals on the Periodic Table.

The rich coordination chemistry of sulfate combined with U(IV) and Ce(IV) has yield fascinating ‘superatoms’, the M_{70}-torroid (M=U, Zr, Ce), and supramolecular assembly of these clusters, with use of polyvalent countercations (transition metals and lanthanides). Dissolution of these clusters in organic media leads to different assemblies in solution altogether, studied by small-angle X-ray scattering.

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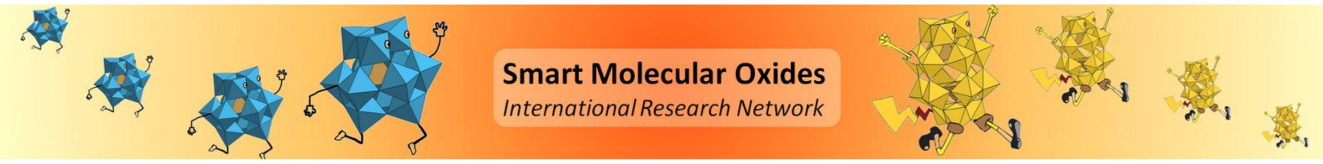
Keynotes



How IPAs are made? The answer to Mo, W, V, Nb and Ta IsoPolyAnions from the POMSimulator

Enric Petrus, Mireia Segado, Carles Bo

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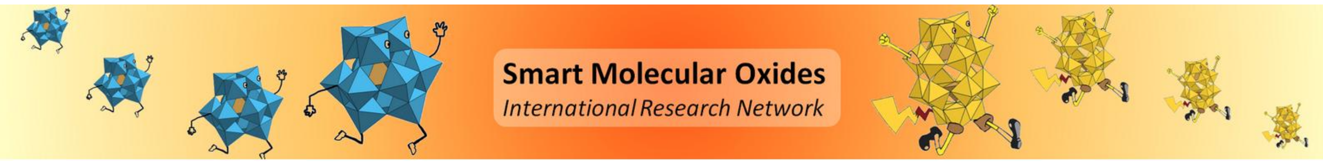
POMSimulator enables dealing with multi-species multi-equilibria systems in a rather pragmatic manner and relaying on quantum mechanics based methods automatically. By considering any set of species possibly existing in solution, our new method builds reaction networks and produces

simple speciation diagrams (% species vs pH) and also phase speciation diagrams (total metal concentration vs pH) in excellent agreement with available experimental data. Moreover, those new algorithms provide

an unique way to unravel the intrincate nucleation mechanisms in play to form larger clusters. This talk will highlight features and limitations of latest POMSimulator version. The first applications to Mo and W, and to V, Nb and Ta isopolyanions will be presented.



CHARGE MODULATION IN PD-BASED OXO-CLUSTERS AND THEIR USE IN HETEROGENEOUS CATALYSIS

Saurav Bhattacharya and Ulrich Kortz*

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Polyoxometalates (POMs) based exclusively on Pd^{2+} ions (polyoxopalladates, POPs) were discovered in 2008.[1] The area of POP chemistry has developed rapidly ever since due to the fundamentally novel structural and compositional features of POPs resulting in unprecedented electronic, spectroscopic, magnetic, and catalytic properties.[2] We have also developed strategies to design POP-based heterogeneous catalysts via: (a) a self-immobilization process wherein the POPs are organically functionalized and utilized as secondary building units (SBUs) in the construction of MOFs (POP-MOF)[3], and (b) the encapsulation of POPs in the cavities of known porous MOFs by the insertion of discrete POP clusters in the cavities of MOFs by the solution impregnation method (POP@MOFs).[4] In recent years, our aim has been to suitably modulate the structures of the discrete Pd-based nanoclusters along with their associated charges in order to gain a certain degree of control over the structure-property relationship. This pursuit has led to the discovery of unprecedented neutral palladium-based oxo-clusters viz. the $[Pd_{16}O_8(OH)_8((CH_3)_2AsO_2)_8]$, $\{Pd_{16}\}$, it's chlorido derivative $[Pd_{16}Na_2O_{10}(OH)_3Cl_3((CH_3)_2AsO_2)_8]$, $\{Pd_{16}Cl\}$, the $[Pd_{24}O_{12}(OH)_8((CH_3)_2AsO_2)_{16}]$, $\{Pd_{24}\}$, and the $[Pd_{40}O_{24}(OH)_{16}\{(CH_3)_2AsO_2\}_{16}]$, $\{Pd_{40}\}$, which is the second largest Pd-oxo cluster isolated till date.[5] We have also demonstrated their effectiveness as precursors to generate size-controlled Pd-nanoparticles immobilized on mesoporous silica supports, thereby leading to effective heterogeneous hydrogenation catalysts for the transformation of various arenes to saturated carbocycles.

References

[1] E. V. Chubarova, M. H. Dickman, B. Keita, L. Nadjo, M. Mifsud, I. W. C. E. Arends, U. Kortz, *Angew. Chem. Int. Ed.* **2008**, *47*, 9542.

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[5] (a) S. Bhattacharya, U. Basu, M. Haouas, P. Su, M. F. Espenship, F. Wang, A. Solé-Daura, D. H. Taffa, M. Wark, J. M. Poblet, J. Laskin, E. Cadot, U. Kortz, *Angew. Chem. Int. Ed.* **2021**, *60*, 3632-3639; (b) S. Bhattacharya, X. Ma, A. S. Mougharbel, M. Haouas, P. Su, M. F. Espenship, D. H. Taffa, H. Jaensch, A.-J. Bons, M. Wark, J. Laskin, E. Cadot, U. Kortz, *Manuscript Submitted*.

HYBRID (ISO)PORPHYRIN – POLYOXOMETALATE MATERIALS

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The development of hybrid polymers incorporating polyoxometalates (POMs) is a promising approach to elaborate new functional materials. To expand the practical applications, their association to a visible-light photosensitizer is needed.

In this context, we have developed a method of electropolymerization of POMs based on nucleophilic attack onto the electrogenerated porphyrin dications.[1] The formation of hybrid POM-porphyrin copolymeric films (Fig. 1, film I) can be obtained by the electro-oxidation of porphyrin in the presence of the POM bearing at least two nucleophilic groups (Nu-POM-Nu, where Nu = py, -NH_2 or –OH). This process is feasible for various type of POMs such as Dawson, Lindqvist, Keggin or Anderson type POMs. [2-4] Stable 3D isoporphyrin – PIM copolymers [5] (PIM = PolyIodoMetalate) have been also develop recently showing interesting efficiency even upon only NIR illumination. A second methodology is also proposed to form hybrid POM-porphyrin films (Fig. 1, films II or III): firstly, there is the formation of cationic polyporphyrin electropolymer. Then, by metathesis reaction, there is the exchange onto the surface of the counter ions by the POM^{n-} [6] or by the nanoparticles stabilized with POM^{n-} (POM^{n-}@*M, M = Ag, Au, Pt*).[7] The photovoltaic performances of these hybrid materials have been investigated. In order to increase the efficiency, mesoporous ITO electrodes have been also used (Fig. *1, bottom right*).

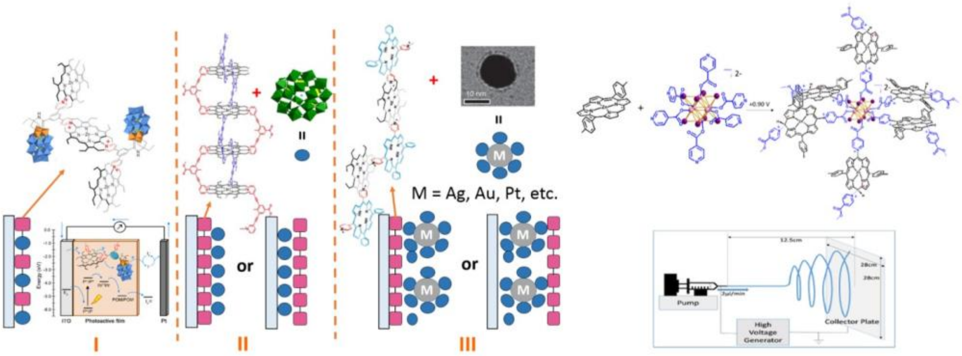

Figure 1. Various type of porphyrin-POM films. Bottom right: electrospining configuration used for deposition of ITO nanofiber layers.

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HETEROGENEOUS ELECTROCATALYTIC WATER OXIDATION WITH POLYOXOMETALATES

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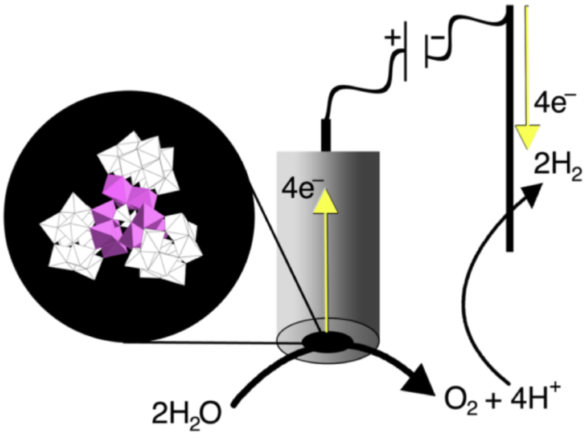
Water oxidation is considered the bottleneck to develop an efficient and cost-effective water splitting technology. State-of-the-art water electrolyzers are still far from being competitive for hydrogen production from fossil fuels, given the cheap and well-established production scheme. One of the challenges resides in substituting the expensive noble metal catalysts by earth-abundant counterparts while maintaining the efficiency and performance required for technological applications. The requirements for catalyst development bring additional challenges beyond performance, since the materials must be robust and active in the (typically extreme) working conditions: pH, high current densities, high oxidation potentials, nascent oxygen, etc.

Polyoxometalates are excellent redox catalysts, and typically show great stability in oxidation conditions. However, during water oxidation, this intrinsic stability is jeopardized by the solution equilibria, where the small fraction of free metal cations, in equilibrium with the POM structure, are prone to precipitate as metal oxides, also efficient water oxidation catalysts.[1] One plausible solution was found in the processing of POMs as heterogeneous solid-state catalyst, where the equilibria in solution is neglected.[2] In this contribution we will present the advantages and disadvantages of this approach., along future trands to bring POM-based water oxidation catalysts further on the road to relevant technological applications.



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CHAOTROPIC EFFECT AS MOTIF ASSEMBLY IN POM CHEMISTRY

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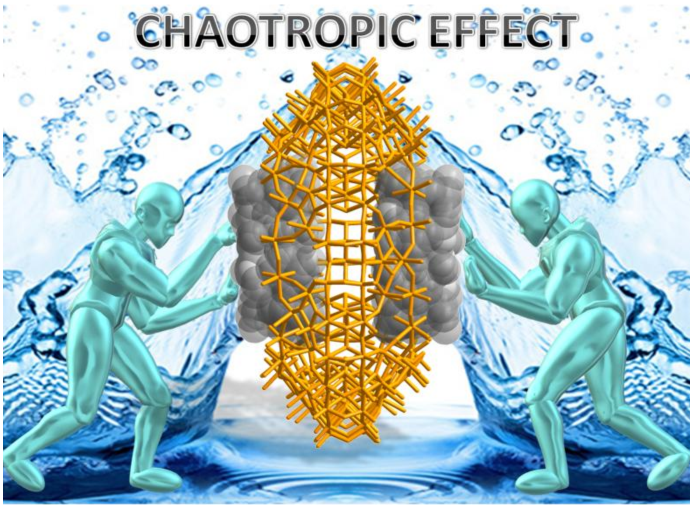
Following up on reports on interactions of conventional chaotropic anions (SCN^-, ClO_4^-...) with non-ionic organic entities (proteins, macrocyclic hosts, micelles...), the chaotropic effect has recently emerged as a generic driving force for supramolecular assembly. This water-mediated effect becomes extremely effective for large inorganic polyanions such as the polyoxometalates (POMs).

This talk will review our recent findings demonstrating the mastering of the chaotropic effect offers innovative avenues i) to control the polycondensation of metalate ions,[1,2] ii) to design redox-responsive host-guest systems,[3,4] iii) to construct highly ordered hybrid systems with large cavities, and iv) to self-assemble POM with non-ionic surfactants into membrane-like organizations.



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DIGITAL DISCOVERY OF MOLECULAR METAL OXIDES AND CHEMPUTATION

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The reason I started working in the area of ultra large polyoxometalates was because of their complexity, diversity and the observation that these clusters appear to encode more information than is present in the synthesis protocols. That was back in 1999. Since then I've wanted to build robotics not to randomly discover new clusters, but understand and account for the information embedded into the structures. In this talk I will describe this journey and how the use of programmable digital robotics has allowed us to explore chemical space, more specifically, molecular metal oxide chemical space searching for new clusters, properties, and applications.

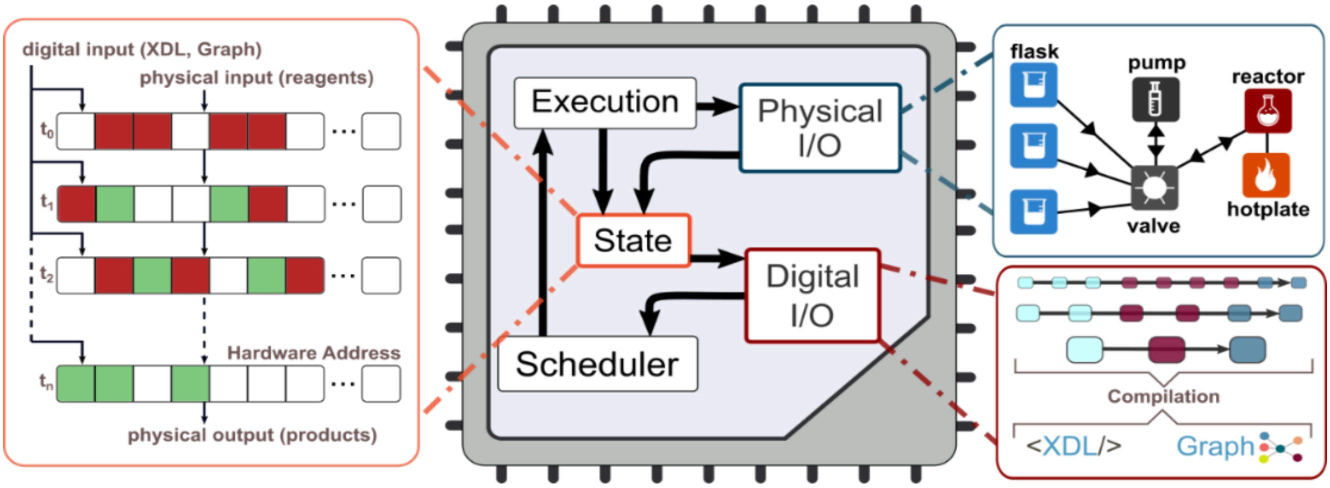

Figure caption Scheme showing how a digital program (left) can be used to set up an automated system that runs like a computer using a state machine (middle) operating simple robotics to do synthesis (right).

EVOLUTION OF {MW$_5$} LINDQVIST POM SYNTHESIS

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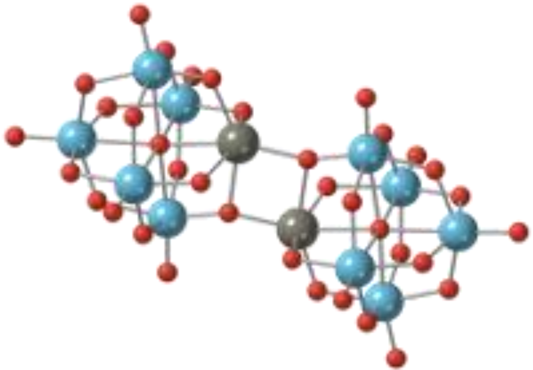
In 1968, Jahr, Fuchs and Oberhauser were the first to prepare $(TBA)_2[W_6O_{19}]$ during an extended investigation of the alkaline hydrolysis of metal alkoxides, [1] and the structure was determined soon afterwards. [2] Subsequently, we showed that group 4 and group 5 transition metals can be incorporated into this fundamental POM structure by careful hydrolysis of metal alkoxide mixtures, [3] which paved the way for systematic studies of homologues, [4] and comparative catalytic investigations. [5]

Analogues of {MW$_5$} POMs containing later first-row transition metals are expected to show interesting reactivity, but examples remained elusive until we prepared the first {CoW$_5$} derivatives by adapting our non-aqueous hydrolytic approach to POM synthesis. [6] This talk will describe our recent successful efforts to include a wider range of transition metals into {MW$_5$} POMs and extend the methodology to post transition metal derivatives, thereby providing general access to a new series of reactive Lindqvist-type anions. This work has revealed a new and apparently generic {M$_2$W$_{10}$} structural type, as illustrated by the dimeric zinc anion shown below, and ^{17}O NMR has been used to monitor structural evolution following initial base degradation of ^{17}O-enriched $[W_6O_{19}]^{2-}$.



Structure of the anion $[(ZnW_5O_{18}H)_2]^{6-}$

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COMPUTATIONAL STUDY OF THE STAIRCASE MOLECULAR CONDUCTIVITY OF POLYOXOVANADATES ADSORBED ON AU(111)

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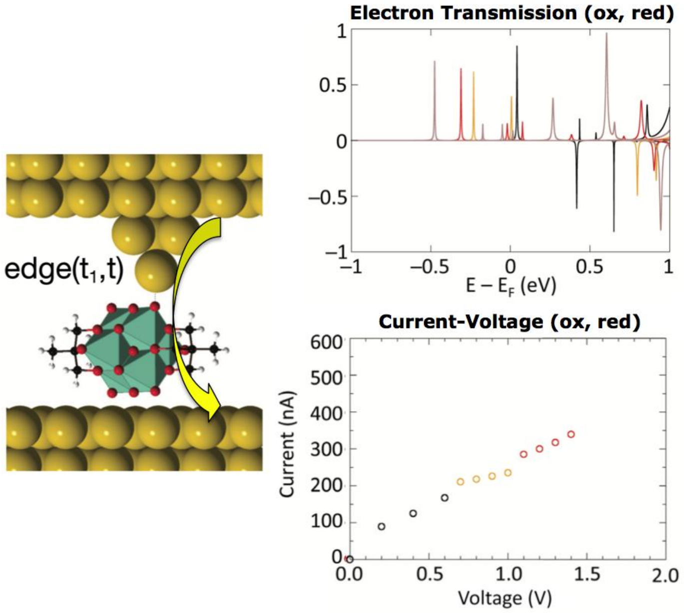
Continuing with the research on POM systems with multiple resistive states,[1] this computational study presents the molecular conduction properties for derivatives of V_6O_{19} and $V_{18}O_{42}$ frameworks,[2] which were targeted as possible successors of the materials that are currently used in complementary metal–oxide semiconductor technology. Molecular conductivity calculations on the Lindqvist-type absorbed on Au(111) shows a staircase conductivity vs. a bias voltage, which depends directly on the oxidation state of the absorbed molecule. After these proof-of-principle calculations we explored $V_{18}O_{42}$, a larger system featuring many more easily attainable redox states and, hence, in principle even more interesting from the multiple-state resistive (memristive) viewpoint. Calculations suggest that the latter molecule does not possess staircase conductivity due to the large number of unpaired electrons in the resting state.



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POLYOXOMOLYBDATES-PEPTIDES CONJUGATES FOR CANCER CELL TARGETING

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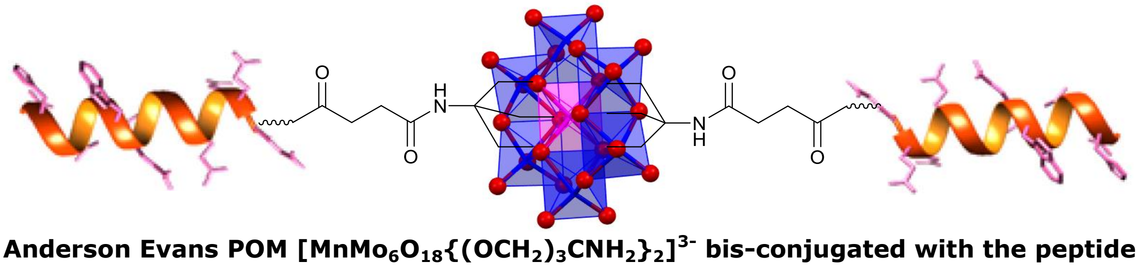
Hybrid polyoxometalates (POMs) can establish a unique interplay of supramolecular interactions with several biochemical targets, often leading to their deactivation [1]. Among the available hybrid polyoxomolybdates, the Anderson-Evans POMs display a promising anticancer activity. The conjugation of such POMs with the antagonist peptide Demobesin-1 (fQWAVGHL-NHEt) was exploited to impart cell targeting capabilities, with the goal to improve their low selectivity [1]. However, the interactions established between the peptide chain and the POM surface have a strong impact and hamper peptide chains availability. Indeed, the POM seems to be responsible for peptide folding and vesicular self-assembly of the resulting hybrids. Within this scenario, the use of tailored spacers to mitigate such interaction has shown to be very useful [2]. Peptides containing either the spacer Ttds=Trioxatridecan-succinamic acid or EEEEβA=Glu-Glu-Glu-Glu-βAla or both were thus used to prepare the corresponding hybrid POMs. The properties of the bio-conjugates were monitored by multiple techniques, including 2D NMR, fluorimetry and Circular Dichroism, and were compared with those of the spacer-free derivative. The presence of both spacers make the peptide more available towards intermolecular interactions. As a matter of fact, the hybrid displays supramolecular assembly into fibres, and a higher (ca. 13% more than spacer-free POM) cytotoxicity against cancer cells.



Anderson Evans POM $[MnMo_6O_{18}\{(OCH_2)_3CNH_2\}_2]^{3-}$ bis-conjugated with the peptide H-D-PheGlnTrpAlaValGlyHisLeuNHEt through tailored spacers.

[1] V. A. Zamolo, G. Modugno, E. Lubian, A. Cazzolaro, F. Mancin, L. Giotta, D. Mastrogiacomo, L. Valli, A. Saccani, S. Krol, M. Carraro, M. Bonchio *Front. Chem.* **2018**, 6, 278

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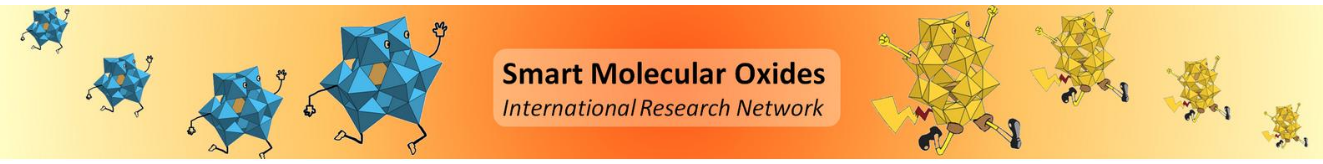

Smart Magnetic POMs for Quantum Computing

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Magnetic POMs provide nice examples of molecular spin qubits for quantum computing [1, 2]. In this talk I will show some recent advances in this area both from the point of view of the design of POMs showing the ability to isolate in a single molecule several spin qubits, and from the point of view of addressing these spin qubits using an electric field.

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Oral Communications

UNUSUAL REACTIVITY VIA POLYOXOTUNGSTATE FUNCTIONALIZATION

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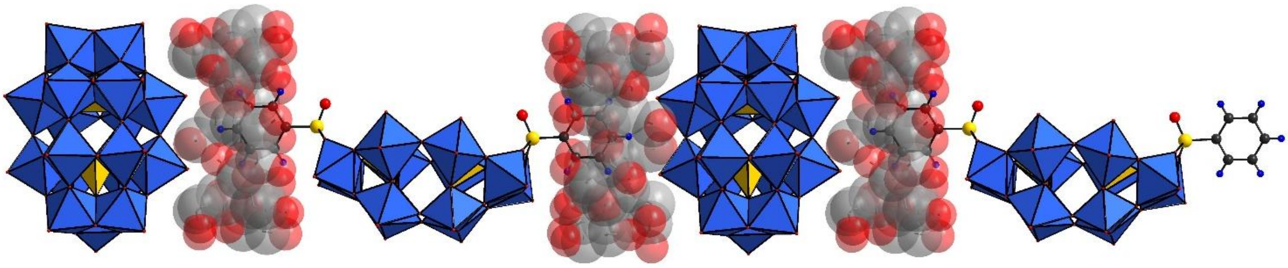
Functionalization of polyoxometalates (POMs) with organophosphonate and -arsonate moieties enables not only stabilization of otherwise highly labile POM architectures, but also the design of novel POM precursors leading to solution-stable heterometal POM derivatives with unusual structures and interesting electrochemical and magnetic properties.[1],[2],[3]

Here we illustrate the above by the results obtained during the reactivity studies of some organophosphonate-functionalized POM derivatives towards transition metals and lanthanides as well as in self-assembly reactions of POM-based supramolecular assembly with α-cyclodextrine.



Supramolecular interactions allow the co-existence of lacunary $\{P_2W_{12}\}$ and complete Wells-Dawson polyanions.

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ELECTRON-RICH POLYOXOMETALATES FOR ENERGY STORAGE APPLICATIONS

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The constantly growing demand in renewable energy sources brings the need of new methods to store this energy that can be released when demand exceeds generating capacity. Storage of energy as electrical charge in batteries and storage of energy via the conversion into chemical fuels are the two most promising solutions to this challenge. Polyoxometalates (POMs) are ideal candidates in this regard due to their ability to reversibility accept multiple electrons with no change in their structure.

The study by Awaga and co-workers suggested that the Keggin-type POM, $[PMo_{12}O_{40}]^{3-}$, can undergo to reversible 24-electrons reduction in Li ion batteries.[1] Recently, it has been revealed that the Wells-Dawson anion, $[P_2W_{18}O_{62}]^{6-}$ undergoes to extensive reduction and can be used for rapid H_2 generation or as an electrolyte in a high energy-density redox flow battery.[2] Although a various number of works have reported charge storage and conversion materials based on electron-rich POMs, the formation of 'super-reduced' POMs by chemical reduction neither in solid state nor in solution has hardly been investigated. This prompt us to explore the step-wise chemical reduction of POMs in order to provide better fundamental understanding of the reactivity and the electronic properties of the resulting electron-rich nanoscale metal oxides as well as the use of them for energy applications.

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COMPUTATIONAL INVESTIGATION ON THE ROLE OF POMS IN THE CO_2 PHOTOREDUCTION CATALYZED BY (POM,CAT)@MOF/POP COMPOSITES

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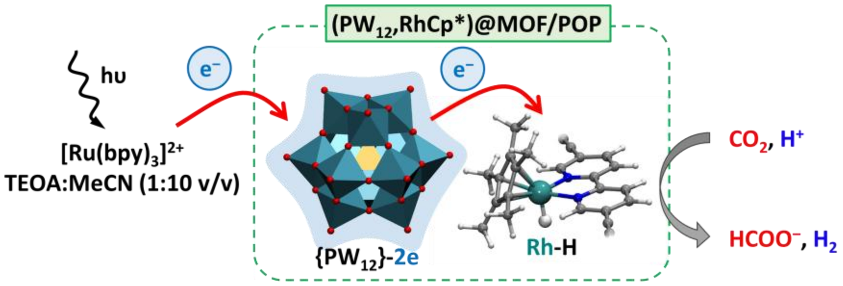
The catalytic activity of a Rh-based catalyst (namely RhCp*) for CO_2 reduction immobilized inside a UiO-67 MOF was found to be significantly enhanced by co-encapsulating a Keggin-type $[PW_{12}O_{40}]^{3-}$ POM (PW_{12} for short) inside the material.[1] However, the reasons for such an enhancement remained obscure. Here, we conducted a detailed computational analysis aimed at understanding the participation of the POM in the reaction mechanisms governing the reduction of CO_2 into formic acid as well as the H_2 evolution process, which is the main side-reaction, and how it relates with the experimentally observed activity. Our DFT calculations revealed that under photocatalytic conditions, the POM acts as an electron relay, assisting the formation of the active form of the catalyst while preventing the formation of a highly stable intermediate. Notably, this results in a reduction of the overall free-energy barriers and in turn, in an acceleration of the reaction rates. Moreover, we have carried out Molecular Dynamics (MD) simulations to investigate the selectivity shift in favor of H_2 observed experimentally when the same catalytic system is immobilized inside a porous organic polymer (POP) instead of inside a MOF.



Schematic representation of the role of PW_{12} in the photocatalytic CO_2 reduction by $(PW_{12},RhCp^*)$@MOF/POP materials

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STORAGE OF ELECTRONS AND PROTONS ON METALLA-SILOX POLYOXOMETALATES

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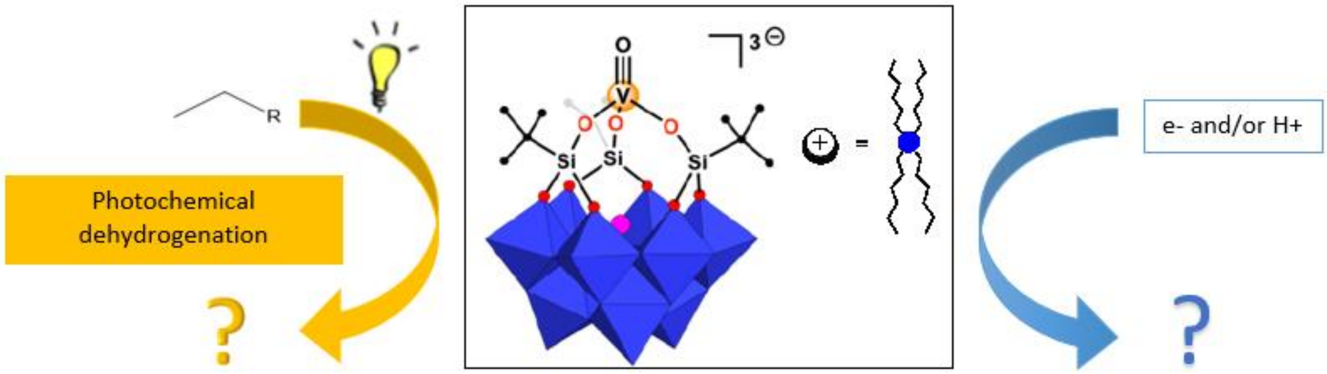
The ability of polyoxometalates to act as multielectron acceptors is exploited in the context of solar energy conversion. Yet this approach usually requires the association of the POM to a visible-range antenna.[1] POMs also absorb in the UV part of the spectrum and could act as ideal photocatalysts.[2] In recent years the decatungstate $[W_{10}O_{32}]^{4-}$, used as a tetrabutylammonium salts, has thereof found wide applications in the catalytic photochemical functionalization of alkanes.[3]

Our approach is based on the utilization of silox POMs and their metallic derivatives as potential photocatalysts (Figure).[4] [5] The main idea is to couple in a single system the photochemical capacity of POM framework (to promote hydrogen atom transfer) in tandem with single electron transfer (SET) chemistry of early transition metal from the first row. In this presentation we will discuss our preliminary results on the behaviour of the mono and bi-reduced derivatives of a vanadium-oxo polyoxometalate, in presence of protons. This work is part of a more general topic dealing with alkane photochemical dehydrogenation. Example of photochemical activation of alkane in presence of vanadium-oxo polyoxometalate will be also discussed.



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DEVELOPMENT OF NOVEL SUPRAMOLECULAR ASSEMBLIES BASED ON PROTEINS AND POLYOXOMETALATES

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Supramolecular interactions are a key aspect of the biological functions of proteins allowing them to reversibly bind to specific substrates and to self-assemble into complex superstructures. However, controlling the formation of protein supramolecular assemblies to develop novel biomaterials and gain a deeper understanding of the self-assembly process remains a challenge so far.[1] Nevertheless, hybrid polyoxometalates (POMs) could be used in order to achieve controlled protein assembly since POMs are known to interact with proteins, they are highly tunable in terms of their physical and chemical properties and protein-binding ligands can be attached onto the POM further promoting directed supramolecular interactions. In this respect, biotin is a particularly interesting ligand since it binds to certain proteins, such as avidin, with one of the highest known affinities.[2] Hence, biotin-grafted POMs and avidin, which has four available binding sites, can be used as building blocks for the formation of POM-protein supramolecular assemblies with the POM serving as a rigid inorganic linker between proteins (Figure 1). As a result, various bis-biotinylated POMs based on the Anderson-Evans ($MnMo_6$) and the Lindqvist (V_6) structures were synthesized. Different binding interactions were observed via fluorescence, UV-Vis, and CD spectroscopy depending on the length of the linker between biotin and the POM core. Moreover, POMs with enough separation between the biotin moieties (~18 Å) gave rise to a POM-linked network of proteins with 2:1 (POM:avidin) binding. Furthermore, these binding interactions produced large particles in solution as determined by DLS and TEM.

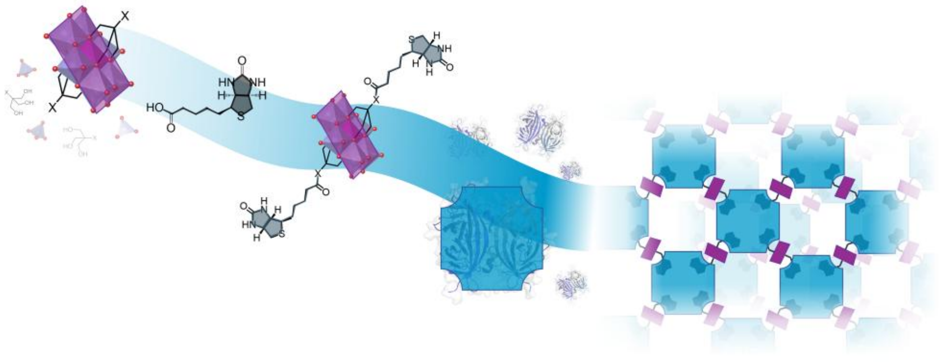

Figure 1: Schematic representation of the Anderson-Evans ($MnMo_6$) structure bis-functionalized with biotin and then combined with biotin-binding proteins to form POM-protein supramolecular assemblies (bottom right). $MnMo_6$ POM core in purple, organic moieties in black and proteins represented by blue squares.

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ELECTROCATALYTIC WATER OXIDATION BEGINNING WITH POMS: DISTINGUISHING BETWEEN HOMOGENEOUS AND HETEROGENEOUS CATALYSIS

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Polyoxometalates (POMs) are molecularly defined complexes that can be substituted to contain redox or catalytically active metals such as Co, Ni, Fe, or other transition metals. These complexes have been extensively explored as homogeneous catalysts for water oxidation—including electrochemically driven, solution-based water oxidation [1]. However, the hydrolytic and oxidative instability of these complexes can lead to the formation of heterogeneous metal oxides that are highly active towards electrocatalytic water oxidation, the heterogeneous phase often generating electrocatalytic current >700 times greater than the electrocatalytic current from the POM precursor [2]. This means that even 1% decomposition of the POM precursor into heterogeneous metal oxide can lead to significant electrocatalytic current, which can be mistakenly attributed to the original POM. Distinguishing between true, homogeneous POM-based catalysis and heterogeneous catalysis from metal oxides derived from the POM precatalyst is, therefore, a difficult analytical problem especially considering that both the POM and metal oxide can have contributions to the total electrocatalytic current and the observed current is a linear combination of the two concurrent pathways. The approach to delineating the current contributions from all of the species involved uses the method of multiple alternative hypotheses and disproof thereof. In this oral presentation, I will outline the primary and alternative hypotheses for the kinetically dominant water oxidation catalyst under electrochemically driven conditions. Furthermore, I describe the general route for quantitative analysis of POM stability, kinetic competence of the possible catalysts, and means to disprove contributions of heterogeneous phases to the observed catalytic current—all in route to developing next generation water oxidation catalysts.

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MESOMORPH POLYOXOMETALATE-BASED HYBRIDS MATERIALS FOR PHOTONICS

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The control of the molecular organization in semiconducting thin films is a key point for improving their optoelectronic performances[1]. For instance, self-organization of electron donor (D) and acceptor (A) moieties into highly ordered molecular architectures is extremely promising for optoelectronic applications.[1] In the search for alternative molecular electron acceptors, polyoxometalates (POMs) are emerging in areas related to energy conversion/storage and information technology owing to their remarkable electron reservoir properties[2,]. In this context, we are developing hybrid systems combining acceptor oxoclusters to donor mesogenic π-conjugated moieties and aliphatic chains in a unique molecular architecture. The antagonistic chemical nature of the inorganic and organic parts should lead to nanosegregation of both units into mesomorphic structures characterized by the formation of distinct regularly alternated D and A subdomains.

We will herein describe the first mesogenic donor-acceptor POM-based hybrid[3] (Fig.1). In this presentation we will develop, the synthetic strategy of the hybrid system as well as its structural characterization in the solid-state and the preliminary photophysical studies.

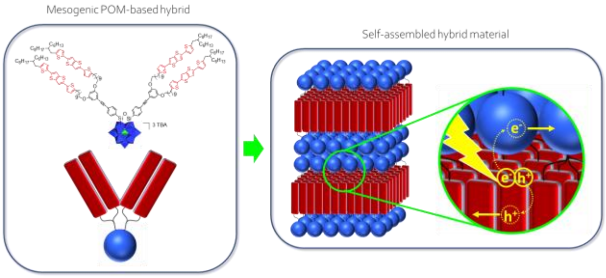

Figure 1: Schematic representation of the target molecular architectures and their self-assemblies into multi-lamellar nanostructures intermingling electron and hole conduction channels

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Improving The Electrocatalytic Activity And Stability Of Prussian Blue Analogues By Introducing Au NPs

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Prussian blue analogues (PBAs) have been proven as excellent earth-abundant electrocatalysts for the oxygen evolution reaction (OER).[1,2] Interestingly, further improvements can be achieved by increasing their electrical conductivity,[3] but scarce attention has been paid to quantify the electroactive sites of the electrocatalyst when this enhancement occurs. In this work,[4] we have studied how the chemical design influences the specific density of electroactive sites in different Au–PBA nanostructures. Thus, we have first obtained and fully characterized a variety of monodisperse core@shell hybrid nanoparticles of Au@PBA with different shell sizes. Their catalytic activity is evaluated by studying the OER, which is compared to pristine PBAs and other Au–PBA heterostructures. Interesting improvements are observed only for the core@shell heterostructures mainly due to the high contact between both compounds, the increase of the conductivity of the hybrid material and the PBA shell which prevents Au from its oxidation. This strong synergistic effect evidences the importance of the chemical design for preparing PBA-based nanostructures exhibiting better electrocatalytic performances and higher electrochemical stabilities.

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THE DECANIOBATE AS PRECURSOR FOR POLYOXONIOBATES

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POM chemistry with group V (Mo, W) is very diverse and different species with different sizes have been isolated in a wide range of pH. Niobium chemistry is more limited and mostly dominated by the Lindqvist hexaniobate $\{Nb_6\}$ in high pH aqueous solution.

However, we found decaniobate $\{Nb_{10}\}$ could be a very promising reactant and building block to extend the family of polyoxoniobates (PONbs). We were able to stabilize $\{Nb_{24}\}$ units in aqueous solution by simply mixing TMA-$\{Nb_{10}\}$ in presence of alkali chloride [1]. SAXS studies revealed the nature of the alkali impacts directly on the size of the oligomer and its conversion rate. The use of alkali carbonate also leads to disassembly of $\{Nb_{10}\}$ species in $\{Nb_7\}$ units to either form $\{Nb_{24}\}$ derivatives compounds or a new $\{Nb_{10}\}$ stabilized by carbonate groups [2]. This conversion of $\{Nb_{10}\}$ only appear in aqueous solution. Indeed, similar study have been performed in methanol solution and the decaniobate unit remains intact and crystallizes as inorganic frameworks of alkalis and $\{Nb_{10}\}$ with TMA molecules as counterions [3]. The size of the alkali is directly correlated to the dimensionality of this framework: 1D with Li and Na, and 2D with K, Rb and Cs. A 3D architecture was also created with alkali earth cations.

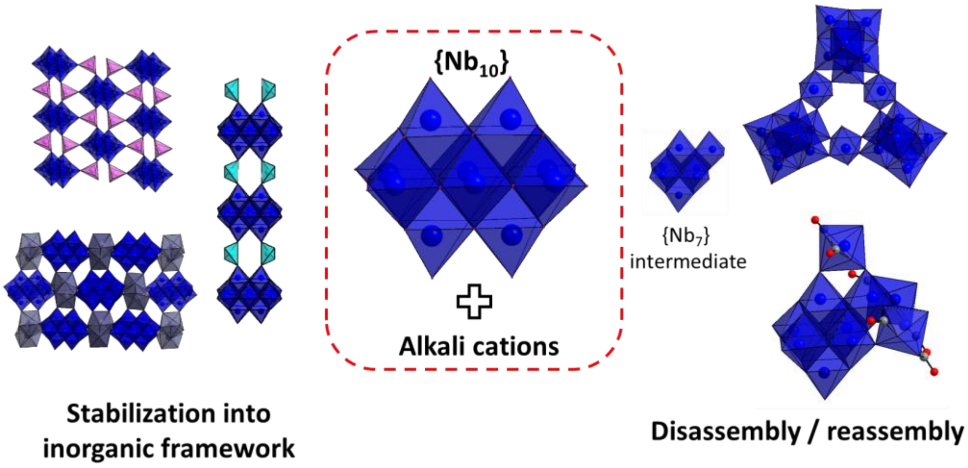

Figure 1. Mixture of TMA-$\{Nb_{10}\}$ with alkalis leads to various PONbs as inorganic frameworks or molecular species.

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COMPUTATIONAL CHEMISTRY AND MOLECULAR METAL OXIDES

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In 2011, Laia Vilà-Nadal received her PhD from the Rovira i Virgili University (Spain), public higher education institution of Southern Catalonia with Prof JM Poblet and Dr Rodriguez-Fortea. She carried out a post-doctoral research at the University of Glasgow with Prof Cronin. Since 2015 she worked as Senior researcher and research Group Co-ordinator in the Cronin Group. She took up a Lectureship position in Glasgow in 2019. She is currently supervising 2 PhD students working on computational modelling of molecular metal oxide clusters for applications in electronic devices, porous materials and designing bio-inspired catalysts. Computational exploration of the space generated by the self-assembly of known molecular metal oxides and the ability to predict new architectures is a challenging task. In my group we are investigating a new family of all inorganic pore materials named POMzites as a proof of concept.[1] Initially, new topological structures will be targeted but pure inorganic systems will be preferred. POMzites are composed of a tungsten ring-formed blocks connected with metal linkers to form a zero to three-dimensional frameworks metal.[2] Our idea is to speed up the discovery of new molecular metal oxide materials using inverse design approaches.

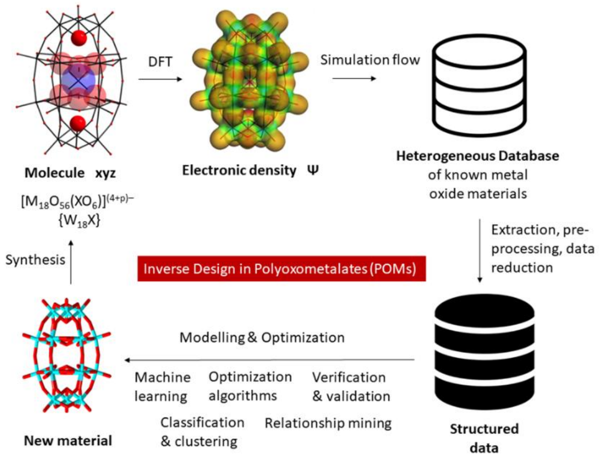

Figure 1: Description of the optimized workflow for achieving inverse design in metal oxides. The coordinates of the known molecules are the starting point to generate their ground-state electron density using density functional theory (DFT) methods. Theoretical calculations are used to generate the data points for a structured database combined with an evolutionary design strategy, targeting new metal oxide materials with specific properties.

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MECHANISM OF NITRITE REDUCTION ELECTROCATALYZED BY POLYOXOMETALATES

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Growth of the renewable electricity production has recently spurred renewed interest in electrochemical methods for electrocatalytic removal of nitrate and nitrite from polluted water. [1] However the development of noble metal-free electrocatalysts, which allow selective and energy-efficient reduction of nitrate and nitrite into harmless or industrially usable compounds is still a challenge. Due to their tunable redox chemistry and the stability of their redox states, polyoxometalates (POMs) are promising electrocatalysts for nitrate and nitrite reduction. [2]

Here we combine electrochemical and differential electrochemical mass spectrometry (DEMS) measurements with microkinetic simulations to identify the reaction products depending on the applied potential and on the pH of the solution and propose a tentative mechanism of the nitrite reduction catalyzed by a series of Keggin POMs, $PW_{12}O_{40}^{3-}$, $SiW_{12}O_{40}^{4-}$ and $BW_{12}O_{40}^{5-}$. DEMS analysis showed the formation of NO at the first one-electron reduction wave of the POM and N_2O at the second POM reduction wave. By using microkinetic simulations of the current-potential curves, the rate constant of the reaction k_c between the reduced POMs and HNO_2 or NO_2^- in solution is obtained and the parameters influencing the catalytic activity and selectivity are discussed.

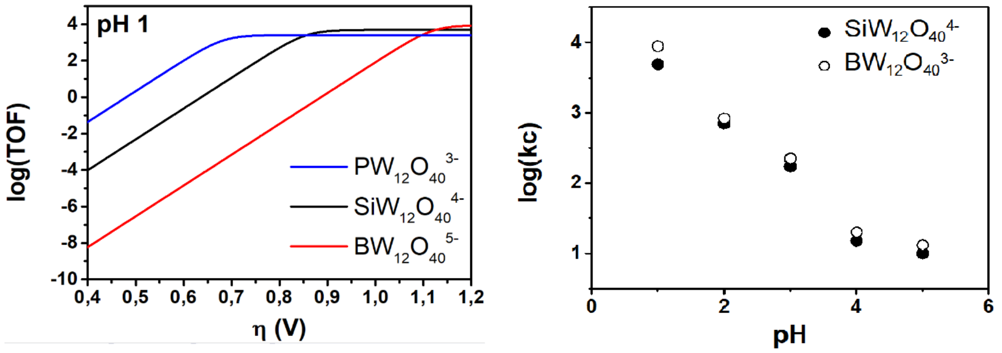

Figure 1. Left: Turnover frequency (TOF) as function of overpotential at pH 1. Right: Influence of pH on the second order kinetic constant (k_c). [3]

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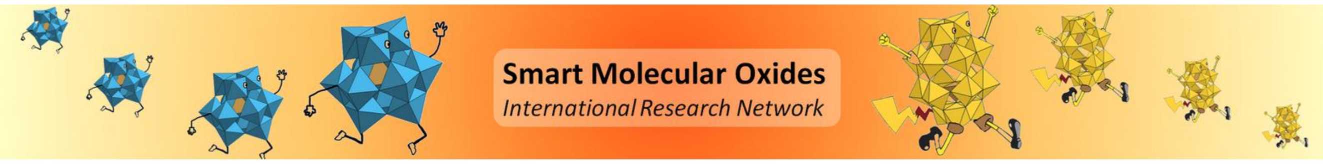

HYDROLYSIS OF INSOLUBLE PROTEINS BY ZR-SUBSTITUTED POLYOXOMETALATES

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Membrane proteins represent about 30% of known proteins and their structural investigation is essential since they are the main targets for many drugs. ([1], [2]) However, their hydrophobic nature, poor solubility, large size and complexity, hampers their analysis in proteomics. In particular, fragmentation of membrane proteins into smaller fragments which are suitable for mass spectrometric analysis is a challenging task, as it requires addition of surfactants in order to solubilize them. However, the proteolytic enzymes typically used in proteomics tend to denature in surfactant solutions. Therefore, investigation of new catalysts which are able to hydrolyze proteins and retain their activity in surfactant solutions is essential. Recently, our group discovered that metal-substituted POMs can act as artificial peptidases in surfactant solutions, and the hydrolytic activity of several globular, water soluble proteins in the presence of surfactants has been investigated. ([3], [4], [5], [6]) In this study, for the first time, the hydrolysis of a fully insoluble protein, Zein, is reported. Due to its hydrophobicity and poor solubility Zein can be used as a model system for membrane proteins, and its hydrolysis was investigated in the presence of Zr(IV)-substituted Keggin type POM, $(Et_2NH_2)_{10}[Zr(\alpha\text{-}PW_{11}O_{39})_2]$. The appearance of new fragments at lower molecular weight in SDS PAGE chromatography upon incubation with Zr-POM is an indication that hydrolysis takes place. The protein was solubilized with different concentrations of SDS (0.36, 3.6, 8%), and it was shown that hydrolytic selectivity and activity strongly depend on the concentration of surfactant used for the solubilization of the protein. Hence, the characterization of micellar superstructure formation between zein, SDS and the POM were explored using different techniques such as Trp fluorescence and circular dichroism spectroscopy as well as dynamic light scattering and electrical conductivity. The speciation of the catalyst in surfactant solutions was also followed by ^{31}P Nuclear Magnetic Resonance Spectroscopy providing insight into its stability under reaction conditions.

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NEW GENERATION OF HYBRID BISPHOSPHONATE POLYOXOMETALATE GOLD NANOPARTICLES FOR BIOMEDICAL APPLICATIONS

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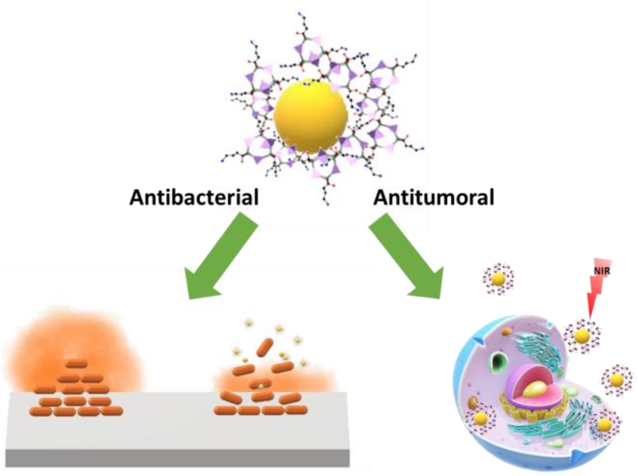
Gold nanoparticles (AuNPs) are amongst the state-of-the-art actors for biomedical applications because of their low toxicity and easy functionalization with a therapeutic agent allowing the facilitation of cellular internalization of the active agents. Additionally, they allow combinatorial therapy to reach an optimized global therapeutic effect. Polyoxometalates (POMs) not only possess antitumor and antibacterial activity but can also be used as reducing and protecting ligands for the preparation of metallic nanoparticles. In this presentation we report two examples of the elaboration of POMs decorated gold nanoparticles for biomedical applications. In the first example, a reduced polyoxovanadate functionalized with bisphosphonate molecules was synthesized and used to prepare in one step hybrid organic–inorganic polyoxometalate decorated gold nanoparticles. These new composites were shown to strongly inhibit *P. aeruginosa* and *S. epidermidis* biofilm growth, with the three components constituting the nanoparticles (Au^0 core, vanadium and alendronate) acting synergistically [1]. In the second example, polyoxomolybdates functionalized with zoledronate were used to decorate spherical gold nanoparticles. These last POM decorated AuNPs provided a combined antitumor activity through drug delivery and photothermal therapy with in vitro inhibition of the proliferation of prostate cancer cells (PC3) in a dose-dependent manner[2].



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POLYOXOMETALATES AS INORGANIC LIGANDS FOR THE LEWIS ACID CATALYZED DIRECT AMIDE BOND FORMATION

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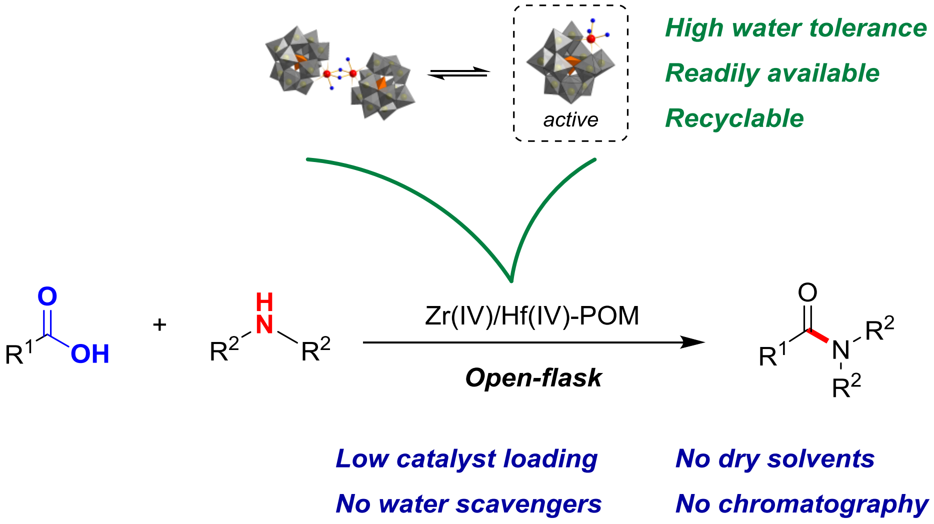
Amide bonds are pivotal structural motifs across all field of chemistry, from biochemistry to medicinal chemistry and materials. However, current methods for the synthesis of amides still challenge modern standards of reaction efficiency, and better catalytic routes are highly desired. Inorganic ligands are frequently overlooked in the development of novel catalysts for organic reactions. Nevertheless, the well-defined structure of polyoxometalates (POM) offer an opportunity to rationally design molecular metal-inorganic ligand catalysts able to enhance organic synthesis sustainability. In this work, Zr(IV)-/Hf(IV)-POM are developed as catalysts for a highly atom-economical synthesis of amides, featuring a broad functional group tolerance, robustness towards the presence of water, and low product/waste ratio [1]. Further, the availability and stability of the catalytic active species are shown to depend on the interplay between the POM ligand structure and the dielectric constant of the reaction medium [2], thereby illustrating insightful design principles that may inspire the development of novel generations of sustainable catalysts based on POM and other inorganic ligands.



High water tolerance

Readily available

Recyclable

Low catalyst loading

No water scavengers

No dry solvents

No chromatography

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REDOX STATE-MODULATED ELECTRON TRANSPORT PROPERTIES OF POLYOXOMETALATES AT THE NANOSCALE

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Polyoxometalates (POMs) are nanometric molecular oxides with remarkable redox properties that can be explored in the context of advanced components [1-3]. We propose to develop scalable functionalities in 2D nanomaterials based on POMs (2D-PN, 2D POM Network) "programmable/switchable" on demand thanks to the multifunctional properties of these molecules (e.g. multiredox states). The first objective is to prepare compact and dense monolayer of POMs on a metal substrate to assess their electron transport (ET) properties. Here, we report the ET properties of those POMs (here $[PMo_{12}O_{40}]^{3-}$ and $[NaP_5W_{30}O_{110}]^{14-}$) in their different redox states using self-assembled monolayers (SAM) and conductive-AFM (Figure 1). For both molecules, we clearly observed an increase of the conductance for the reduced states which is related to a decrease of the energy of the molecular orbital involved in the transport though the metal/POM/metal junction : from ≈0.65 eV to ≈0.43 eV for PMo_{12} and from ≈0.44 eV to ≈0.31 eV for P5W30. We tentatively ascribe this feature to a change from a LUMO mediated ET to a HOMO mediated ET after reduction (ab-initio calculations in progress). Then, we successfully fabricated multi-connected (6 electrodes) hybrid 2D-PN with $[PMo_{12}O_{40}]^{3-}$ and Au nanoparticles (Figure 2) and we measured their ET revealing large variability in the 2D-PN. This measurements will be used to discuss the possible use of these 2D-PN within the global framework of the physical implementation of a neuromorphic reservoir computing system with nano-objects (CNT, nanoparticles, molecules, atomic switches).[4-7]

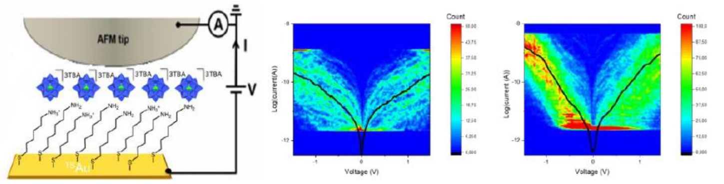

***Figure 1** : General scheme of the electronic transport characterization by C-AFM of the $[PMo_{12}O_{40}]^{3-}$ electrostatically deposited onto alkylamine SAM functionalized gold surface and histogram of the current-voltage curves (I-V) in oxidized state (left) and after one electron reduction (right).*

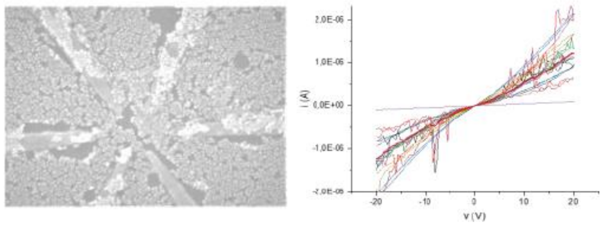

***Figure 2** : SEM images (left) and current-voltage curves (I-V) (right) of fabricated multi-connected hybrid 2D-PN with $PMo_{12}O_{40}$ and Au nanoparticles*

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Molybdenum Reds: Highly Reduced Molybdenum Polyoxometalates Providing Unique Topologies Through *D*- and *F*-Block Ion Incorporation

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This work presents two new classes of highly reduced mix-valence polyoxomolybdates $[\mathrm{Mo}^{V}_{52}\mathrm{Mo}^{VI}_{12}\mathrm{H}_{26}\mathrm{O}_{200}]^{42-}$ $\{\mathrm{Mo}_{64}\}$ and $[\mathrm{Mo}^{V}_{40}\mathrm{Mo}^{VI}_{30}\mathrm{H}_{30}\mathrm{O}_{215}]^{20-}$ $\{\mathrm{Mo}_{70}\}$ constructed by two fundamental type building blocks: $\{\mathrm{Mo}^{V}_{6}\}$ and $\{\mathrm{Mo}^{V}_{2}\mathrm{Mo}^{VI}_{2}\}$. These two frameworks represent new additions to the redefined, and now growing, family of highly reduced polyoxomolybdates: Mo Reds. The $\{\mathrm{Mo}_{64}\}$ cluster displays a super-cube structure composed of a main Mo^{V} framework of truncated cuboctahedron encompassing eight coplanar ring-shaped $\{\mathrm{Mo}^{V}_{6}\}$ building blocks, incorporating 8 Ni^{2+} ions located on the cube vertices and 6 lanthanide ions on the cube face centres. The $\{\mathrm{Mo}_{70}\}$ cluster comprises five tripodal $\{\mathrm{Mo}^{V}_{6}\}$ and five tetrahedral $\{\mathrm{Mo}^{V}_{2}\mathrm{Mo}^{VI}_{2}\}$ building blocks alternatively linked up to form a loop of pentagonal star topology, in which the tripodal $\{\mathrm{Mo}^{V}_{6}\}$ units are further stabilised and linked up by additional molybdate fragments and lanthanide ions. The mechanism of formation and building rules of these new POMs have been investigated and comparisons with known structures were made, greatly enriching knowledge to POM chemistry and offering guidance in design and application of POM materials. In addition, the $\{\mathrm{Mo}_{64}\}$ super-cube has been used in lanthanide enrichment experiments that prove how selective these self-assembly processes are.[1]

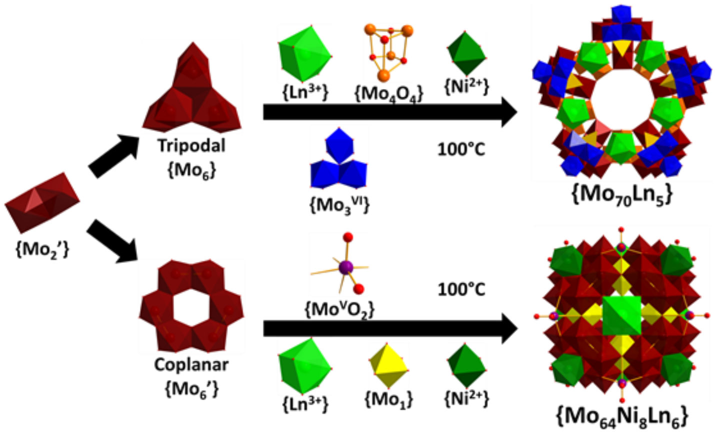

Figure 1. Schematic representation of the formation of the $\{\mathrm{Mo}_{70}\}$ and $\{\mathrm{Mo}_{64}\}$ compounds.

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Posters

NEW PERSPECTIVES WITH LINDQVIST-TYPE HYBRID POMS IN HOST-GUEST SUPRAMOLECULAR CHEMISTRY

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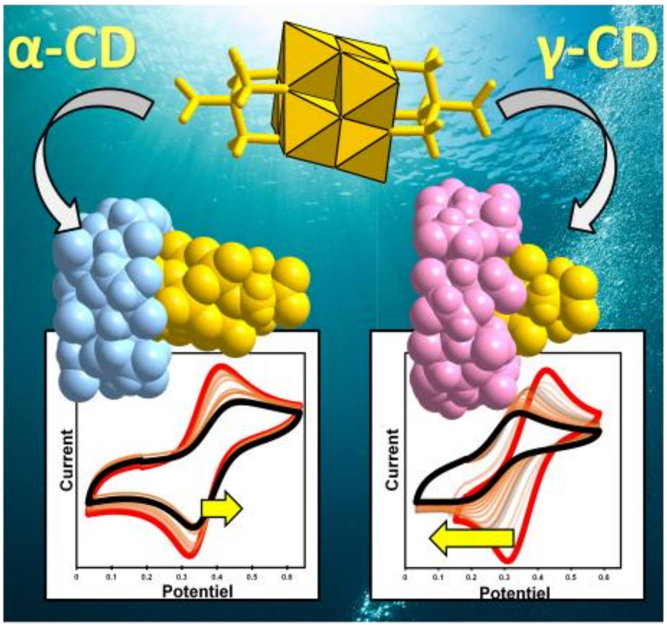
The study of non-covalent interactions involving polyoxometalates (POMs) with organic matter (macrocycles, surfactants, polymers, proteins) is of crucial interest both for fundamental knowledge and for various applications, notably in medicine and materials science. In context, cyclodextrins (CDs) are widely used as drug delivery agents, with a particular interest for developing host-guest systems with POMs. Recent advances in the chemistry of polyoxovanadates (POVs), especially Lindqvist-type hexavanadate compounds, were reported for their relevant applications in energy-related fields. POVs are also promising agents for applications in medicine and their interactions with macrocyclic drug carriers, such as cyclodextrins, have not been reported to date.

In this poster communication, the host-guest chemistry of a series of Lindqvist-type hybrid POVs, $[V_6O_{13}((OCH_2)_3C\text{-}R)_2]^{2-}$ with R = CH_2CH_3, NO_2, CH_2OH and NH(BOC) (BOC= N-tert-butoxycarbonyl) will be discussed in dept. Such supramolecular interactions between POVs and CDs were studied in aqueous solution by NMR, electrochemistry and ITC, as well as in the solid-state (single crystal X-ray diffraction analysis)



MODULAR DESIGN OF NOBLE METAL-FREE MIXED METAL OXIDE ELECTROCATALYSTS FOR COMPLETE WATER SPLITTING

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Transition-metal oxides, especially nickel, copper and cobalt oxides, are widely believed to be potential candidates for robust water splitting electrocatalysts as they are valence-tunable, earth-abundant, cost-efficient and stock-available.[1,2] The anchoring of these catalysts to electrode surfaces is a key challenge to enable long-term stable water splitting performance.[3] Here, we explore the in-situ growth of bifunctional electrocatalysts with outstanding electrocatalytic activity in the full water splitting reaction. The materials reported show high electrical conductivity, chemical tunability, nanostructured morphologies together with excellent long-term stability.

Recently, metal foam electrodes have received wide attention as high surface area supports for electrochemically active materials. [3,4,5] Here, we explore how macroporous Cu foam can be used as a 3D framework for the in-situ growth and anchoring of cobalt tungstate bifunctional electrocatalysts, leading to composites which combine the high electrical conductivity of Cu with the high chemical reactivity of the cobalt tungsten oxide catalyst. Deposition of catalyst nanowires on the Cu electrode is achieved using the hydrothermal deposition of a molecular metal oxide precursor on the electrode surface. Electrocatalytic studies show that the material obtained is a high-performance catalyst for the hydrogen evolution as well as the water oxidation reaction. In consequence, an electrochemical water splitting cell was designed using the identical catalyst composite for both anode and cathode. Initial mechanistic insights, electrochemical performance analyses and stability studies are reported and an initial growth model for the formation of the high-surface area nanowires is described.

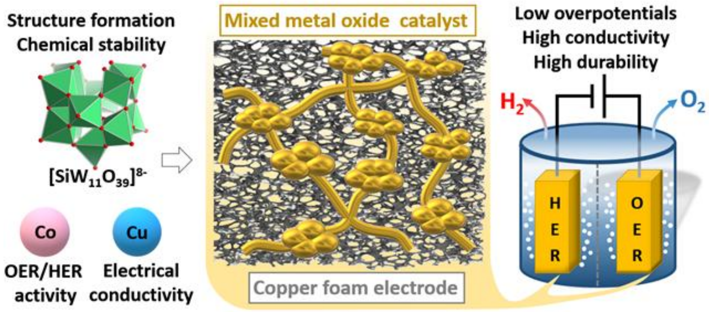

Figure: Synthetic scheme

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SUPRAMOLECULAR HYBRID NETWORKS BASED ON POLYOXOMETALATES AND CYCLODEXTRINS

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Since the emergence of supramolecular complexes based on polyoxometalates (POMs) and cyclodextrins (CD)[1], for which water is the driven force assembling by chaotropic effect, several systems have been proposed[2],[3]. Designing a new class of responsive and adaptable multifunctional materials built from deliberate associations is promising for a large variety of applications (e. g. drug delivery, gas sorption, sensors, etc.).

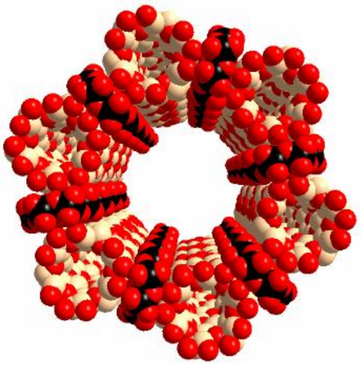

Figure 1 Ball and stick representation of CD-MOFs-Bamboo based on Anderson with αCD

In this context, we proposed to design new extended crystalline POMs-CDs networks, where pore size is tunable, thanks to the diversity of POMs structures. In this case, $[K_3Mo_8^{V}Mo^{VI}O_8S_8(OH)_9(H_2O)]$ polyoxothiometalates and Anderson type POMs were considered as inorganic building blocks interacting with CD external face, while Keggin and Dawson type anions were played the role of specific well-sized isoreticular agents. These entities can exhibit useful abilities for many applications (e. g. catalysis, biological, and redox properties). Besides that, the organic part consists of α, β or γ-cyclodextrins, which are water-soluble torus oligosaccharide derivatives. CDs stacking leads to a well-defined 3D system which can be liken to Kagome lattice or even bamboos, this last related to the channels formed by the CDs internal cavities.

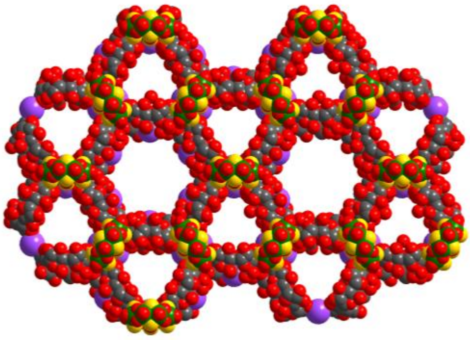

Figure 2 Ball and stick representation of $K_2[Mo_9O_8S_8(OH)_9(H_2O)_5(C_{36}H_{60}O_{30})_2]$.

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Polyoxometalate/Silica-Templated 2D Mesoporous N-P-Carbon Supported Ni clusters/MoC/MoO_2 for Water Oxidation

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Abstract: Electrocatalytic OER is very important in the water electrolysis, which is a key technology for carbon-neutral energy. Here, we report a POM/silica-templated design leading to noble metal-free composite electrocatalysts, which combine high electrical conductivity, high OER reactivity and high durability. By using the cation substituted Keggin phosphomolybdic acid, Ni[$HMo^{VI}{}_{12}O_{40}$] as a precursor, the scalable top-down fabrication allows the stable deposition of Ni clusters/η-MoC/MoO_2 nanocomposites with different functionalities on 2D N, P-doped mesoporous carbon. The composite catalyst shows sustained OER activity in 1 M aqueous KOH over prolonged periods (t >20 h) at low overpotential (η_{10} = 340 mV) and high Faradaic efficiency (>95%). The new synthetic concept will enable the development of multifunctional, (mixed)metal carbide/oxide composites as high-performance electrocatalysts for challenging energy conversion and storage reactions.

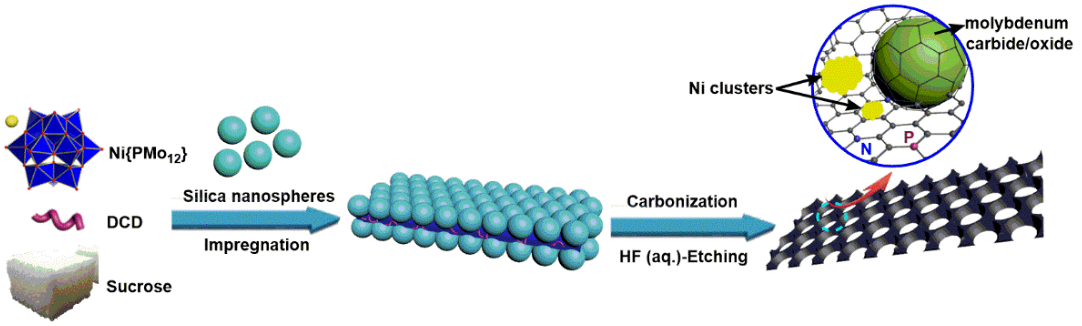

Figure 1 Schematic preparation of the 2D mesoporous Ni clusters/η-MoC/MoO_2/NPC.

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JUBA SAHLI

P5

SYNTHESIS OF NOVEL MW_5 LINDQVIST-TYPE POLYOXOMETALATES

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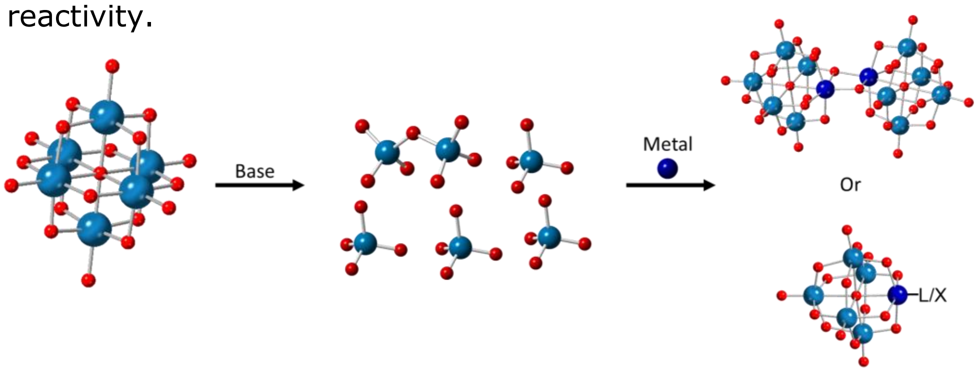
Polyoxometalates containing one or more heterometal are promising catalysts for environmentally important transformations, such as water-oxidation[1] or alkene epoxidation[2]. Examples of such polyoxometalates are common in the literature for the more well-studied polyoxometalates structures, like those based on the Keggin or Wells-Dawson architecture. However, examples based on the smaller Lindqvist unit are rarer.

Herein, we describe a robust synthetic methodology for the synthesis of transition metal substituted $(TBA)_x[MW_5O_{18}]$ Lindqvist-type polyoxometalates, where M= Zn, Co, Fe, and Mn (TBA= tetrabutylammonium). We use a degradative synthetic approach in which $(TBA)_2[W_6O_{19}]$ is treated with base, which in turn reacts with transition metal salts to produce the heterometal-substituted POM.

Both the degradation and reassembly steps were probed using ^{17}O NMR spectroscopy, giving insight into the reaction mechanism and potential intermediates. The products were further characterized by single-crystal X-ray diffraction, cyclic voltammetry, and UV-Vis. DFT calculations were used to give insights into the electronic structure and potential reactivity.



General approach for basic degradation of $W_6O_{19}^{2-}$ followed by reassembly in the presence of heterometals to produce MW_5-type systems.

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SYNTHESIS AND SUPRAMOLECULAR STUDIES OF AN ELUSIVE *POLYOXOPALLADATE* NANO-WHEEL IN AQUEOUS SOLUTION

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Polyoxopalladates (POPs) are a class of self-assembling palladium-oxide clusters that span a variety of sizes, shapes and compositions. One such cluster is $\{Pd_{84}\}^{Ac}$; a 7-fold symmetry wheel constructed from 14 $\{Pd_6\}$ building blocks and lined on the inner and outer torus by 28 acetate ligands.[1] Highly soluble in aqueous solvent, with a hydrophobic cavity and distinct ^1H NMR fingerprint we sought to explore the host-guest behaviour of this unique cluster with small organic molecules. Modelling of the multi-component complexes provided information about size and shape congruity along with identifying possible sites of interaction, compatible systems were then fully analysed by ^1H NMR, DOSY and 1D and 2D NOESY.

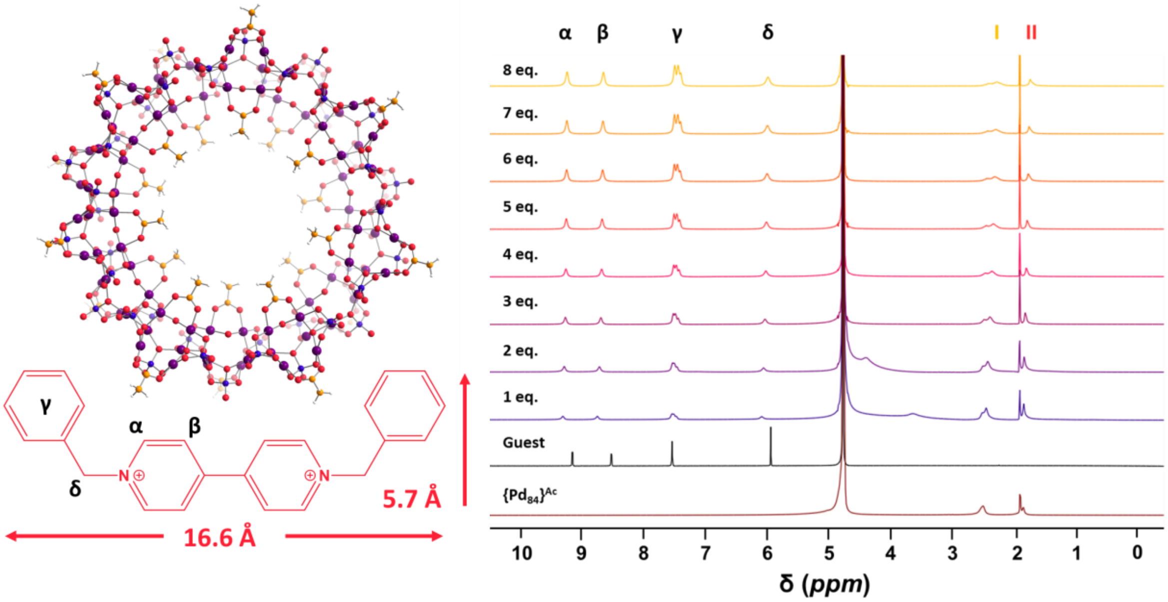

Figure 1: ^1H NMR titration of BVC with 2.48 mM $\{Pd_{84}\}^{Ac}$ in D_2O at 298 K, 600 MHz. $\{Pd_{84}\}^{Ac}$ inner $\{CH_3CO_2\}$; I, outer $\{CH_3CO_2\}$; II.

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POLYOXOMETALATE-SUPPORTED BIOINSPIRED CATALYSTS FOR SMALL MOLECULES ACTIVATION

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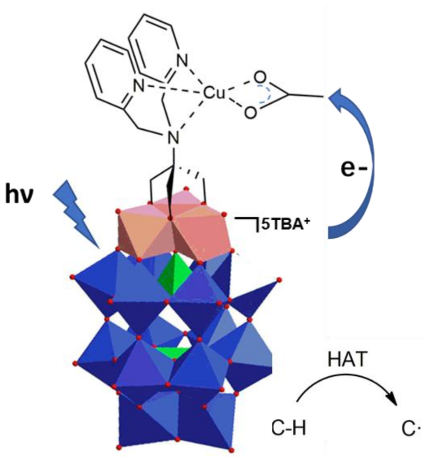
The efficiency of metalloenzymes does not only depend on the first coordination sphere of the metal sites but also on the secondary interactions, and in particular on electrons and protons relays.[1] Polyoxometalates (POMs) are a series of molecular metal oxide clusters which could work as the reservoir of protons and electrons.[2] In the past decades, POMs have been incorporated into hybrid systems by combining them with various inorganic and organic subunits to achieve the electrons and protons communication.[3]–[5]

Our aim is to graft bioinspired complexes onto the POM skeleton to mimic the metalloenzymes. Multidentate organic ligands at the POM surface will provide the first coordination sphere, while the POM could provide the required secondary interactions to induce or improve reactivity.

I will present the platforms obtained via covalently grafting of the ligands (N, N-bis(2-pyridylmethyl)-N-propargylamine) and their characterization, some complexes thereof and reactivity.



Proposal mechanism to the photoredox process of the covalent grafted POM complex

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GROUND-STATE CHARGE TRANSFER IN VANADIUM-CONTAINING POLYOXOMETALATES WITH PHTHALOCYANINATO LANTHANIDE IONS

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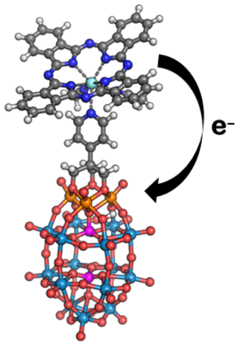
The synthesis, structural characterization, and charge transfer studies of new organic-inorganic hybrid assemblies consisting of electron-donating lanthanide monophthalocyaninato (LnPc) moieties and electron-accepting fully-oxidized polyoxometallates (POMs) have been performed. The LnPc and POM units are linked to each other either by a suitable organic spacer (**1**, POM = $\{V_3\}$-substituted Wells-Dawson)[1] or by direct covalent interaction (**2a** and **2b**, POM = $\{V_{12}\}$-polyoxovanadate).[2] The results of electronic paramagnetic resonance (EPR) spectroscopy, SQUID magnetometry, X-ray photoelectron spectroscopy (XPS) and magnetochemical calculations indicated the presence of both non-photoinduced *intra*- and *inter*molecular charge transfer from LnPc to POM in the solid state and in concentrated solution, where a partial reduction from V^V to V^{IV} has been detected. The obtained results are especially of high interest for studies of molecular charge and spin effects on electron transport characteristics of POM compounds, their molecular ordering, and electron communication on surfaces. These studies are currently underway in our Laboratory.



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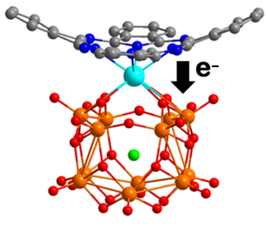

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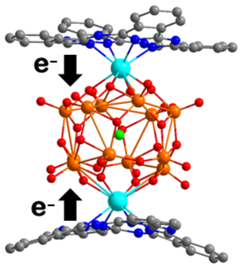

2b

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KEGGIN-TYPE IONS IN THE HOFMEISTER SERIES

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Polyoxometalates (POMs) represent a class of water-soluble metal-oxo clusters built from group V and VI transition metals in their highest oxidation states, e.g. V^{V}, Mo^{VI}, and W^{VI}. This class of compounds exhibits a wide range of structures and chemical compositions which provide diverse properties and make them as useful components in various fields including catalysis, medicine, energy, and materials science. Among the numerous physicochemical properties of POMs, their ability to exchange reversibly electrons is probably the most intriguing and remarkable one, and utilization of POMs in redox processes is now generalized and commonly employed. Otherwise, POMs can also form strong non-bonding interactions with neutral surfaces such as organic macrocycles, micelles, proteins, or polymers. The archetypal Keggin-type heteropolyanions have ability to form step-wise inclusion complexes with the toroidal γ-cyclodextrin macrocycle (γ-CD) in aqueous solution.[1] Such intriguing host-guest association based on this natural cyclic oligosaccharide is shown to be driven by the chaotropic effect and proceeds through water structure recovery process resulting from the desolvation of the interacting units, i.e. POM and cavitand.

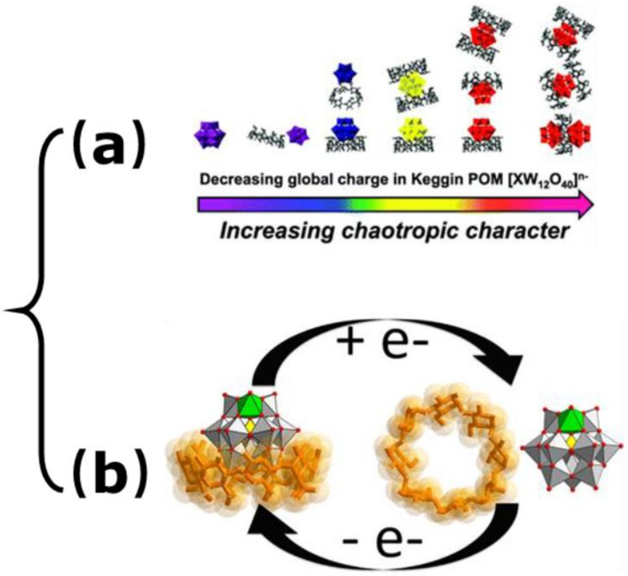

Figure 1. A) illustration of the most representative binding modes involved in the supramolecular assemblies buit from Keggin anions and γ-CD host. B) Structure schematic diagram of the redox-responsive POM@CD complex

In this communication, we will show how the affinity between γ-CD and Keggin-type polyoxometalates $[XW_{12}O_{40}]^{n-}$ anions can be varied with the global charge density of the nanometer-sized polyanion in solution (see Figure 1a). [2] Such results demonstrate that the binding ability of the POMs to γ-CD can be tuned by reversible electron transfer. Moreover, such a study has been expanded using a series of molybdenum and vanadium monosubstituted anions, confirming that the ionic charge corresponds to the main factor in the host-guest process (see Figure 1b). [3]

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