FMOCS IV @ PoCheMoN 2016

Joint Meeting

Frontiers in Metal-Oxide Cluster Science IV
and
Final Meeting of COST Action CM1203
Polyoxometalate Chemistry for Molecular Nanoscience 2016

Programme and Abstracts

10 - 14 July 2016
Newcastle University
Newcastle upon Tyne, UK

COST
EUROPEAN COOPERATION
IN SCIENCE AND TECHNOLOGY

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Welcome to Newcastle!

This joint conference combines the fourth in the “Frontiers in Metal Oxide Cluster Science” series with the final meeting of the COST Action CM1203, PoCheMoN (“Polyoxometalate Chemistry for Molecular Nanoscience”). The first FMOCS meeting was held in Jerusalem in 2010 and was arranged to follow the highly successful international conferences in polyoxometalate chemistry previously held in France, Germany, Spain and Japan. The second and third FMOCS meetings were held in Lanzarote, Spain and in Maffliers, France, the latter of which was joint with PoCheMoN 2014. We hope that this conference is as enjoyable and stimulating as those that have gone before!

A feature of all of the POM meetings has been the vibrant social as well as scientific interactions, and the global POM community has been strengthened as a result. Newcastle is renowned as a friendly city and is a social hub for the region so we trust that we can continue this tradition! There is an opportunity to get to know the city on Wednesday afternoon and in the evening the social and scientific programmes merge as the conference dinner and poster session will both be held at the Discovery Museum, which you will hopefully have a chance to explore.

We are very grateful to Bruker, Advion, CHEM and Chemistry a European Journal for sponsorship of the meeting, please take the opportunity to talk to their representatives (Andrew Gibbs, Andrew Baker, Rob Eagling and Anne Deveson respectively) while they are here.

Thank you for coming - have an enjoyable and stimulating time!

R. J. Errington

John Errington

Lee Cronin

Information for participants

Venue

The conference will take place in the Percy Building, Newcastle University and there will be a reception desk inside the main entrance.
Lectures will be presented in Lecture Theatre **G05** and will also be streamed live to the adjacent Lecture Theatre G13 for non-registered local attendees.

Please wear your badge at all times to show you are a registered participant.

Speakers' presentations

Speakers may use either the local PC in the lecture theatre or their own laptop.

If you wish to use the local PC, please provide your talk to the support team the day before your talk so that we can load all of the talks for each session in advance.

If you wish to use your own laptop, please connect it to the switchbox during the preceding break.

In either case, please **check your slides before the start of your session** to make sure your slides display without any problems.

Internet Access

1. Connect your device to the open wireless network **newcastle-uni-guest**
2. Open a web browser. You will be automatically redirected to the Newcastle University Guest Access Portal login page.
3. Enter the **voucher code** that is included in your welcome pack.

Tea / coffee breaks will be held in the foyer of the Percy Building.

Lunches are **NOT** included in the registration but there are many nearby food outlets. Please see "nearby Places to Grab Lunch" found in your welcome pack.

Smoking

Newcastle University is a smoke-free campus. Smoking is not permitted inside any building and smokers are kindly requested to move off-campus if you wish to smoke.

Luggage storage and Cloakroom

The cloakroom and luggage storage are available in Percy Building G.09/G.10. Please note that any items left here will be left at your own risk.

Emergency Procedures

In the event of a fire alarm, please leave the Percy Building and turn right. Walk through the small arch and congregate outside the front of the Armstrong Building.

Taxis

The recommended local taxi company is: Noda 0191 222 1888

Committees

Organisers

John Errington	Newcastle University, UK
Lee Cronin	University of Glasgow, UK

Scientific Committee

Marcella Bonchio	University of Padova
Emmanuel Cadot	Istitut Lavoisier de Versailles, UVSQ
Eugenio Coronado	ICMol, University of Valencia
Lee Cronin	University of Glasgow
John Errington	Newcastle University
Paul Kögerler	RWTH Aachen
Ulrich Kortz	Jacobs University Bremen
Yang Guang Li	Northeast Normal University, Changchun
Ronny Neumann	Weizmann Institute
Josep-Maria Poblet	Universitat Rovira I Virgili, Tarragona
Anna Proust	Université Pierre et Marie Curie, Paris
Ira Weinstock	Ben Gurion University
Lixin Wu	Jilin University

Local Organisation Committee

Joanne Lakey
Claire Nicoll
Abby Randall
Thompson Izuagie
Kate Phipps
Amanda McGarvy

Contact: chem.events@ncl.ac.uk

Outline Programme

	Sunday 10 July	Monday 11 July	Tuesday 12 July	Wednesday 13 July	Thursday 14 July
		Announcements			
9.00		**K08** C L Hill	**K19** T Parac-Vogt	**K30** G Patzke	**K32** A Proust
15					
30		**C05** P Kulesza	**C13** Carbo	**C21** T Pinto	**C27** Y Wang
45		**C06** R Schreiber	**C14** T K N Luong	**C22** M brahim	**C28** Z Syrgiannis
00 10.00		**K09** S Uchida	**K20** L Wu	**K31** J R Galan-Mascaros	**K33** I Weinstock
15					
30		Tea / coffee break			
45					
00 11.00	Registration	**K10** U Kortz	**K21** L Cronin	**STSM 01-06**	**C29** Peng
15					**C30** P Yin
30		**C07** F Xu	**C15** N Bandeira	**C23** C Gimenez-Saiz	**K34** C Streb
45		**C08** A-L Teillout	**C16** S Reinoso	**C24** H G T Ly	
00 12.00		**K11** M Sokolov	**K22** Y-F Song	**C25** Y Duan	Closing Remarks
15				**C26** W Xuan	
30		Lunch		**Flash presentations**	
45					
00 13.00	Opening Remarks				COST Action CM1203 PoCheMoN MC Meeting
15					
30	**K01** M Bonchio	**K12** R Errington	**K23** E Coronado		
45					
00 14.00	**K02** -M Poblet	**K13** Y Wei	**K24** J Fielden	Historical walk	
15					
30	**C01** L Ruhlmann	**C09** W Ayass	**C17** Q Zheng		
45	**C02** S Roy	**C10** N zarova	**C18** Xie		
00 15.00	**K03** Y-G Li	**K14** C Ritchie	**K25** D Vuillaume		
15					
30	Tea / coffee break				
45					
00 16.00	**K04** C Bo	**K15** R Neumann	**K26** W G Klemperer	Put up posters	
15					
30	**K05** C Boskovic	**K16** O Kholdeeva	**K27** S Polarz		
45					
00 17.00	**C03** B Artetxe	**C11** D-L Long	**C19** P Abramov		
15	**C04** B Bassil	**C12** N Maksimchuk	**C20** Z Lin		
30	**K06** E Cadot	**K17** P Mialane	**K28** H Miras		
45					
00 18.00	**K07** H Nogueira	**K18** R Tsunishima	**K29** P Kögerler	Reception & posters	
15					
30		Reception			
45					

See following details for Tuesday & Wednesday evening events

Arrangements for Tuesday evening

Reception

There will be a drinks reception after the last session on Tuesday evening in the Foyer of the Percy Building at 6.30 pm.

Arrangements for Wednesday afternoon / evening

Historical Walking Tour

There are limited places (30 each) for two Historical walking tours of Newcastle on Wednesday afternoon (1.30 pm to 3.00 pm and 4.00 pm to 5.30 pm).
If you wish to join a tour, please sign one of the lists at the reception desk – Places will be allocated to those who sign up first! Poster presenters should preferably choose the first tour.

Poster Session and Conference Dinner

The conference dinner and poster session will be held on Wednesday evening, July 13th in the Discovery Museum, which is walking distance from the University, past St. James' Park football stadium (see map below).

Poster presenters must put up their posters between 4 pm and 6 pm.

The dinner reception and poster viewing will be from **6 pm to 7 pm** in the Great Hall (guests may also visit other parts of the museum).

Dinner will be served at **7 pm** and poster prizes will be presented at **8.30** pm by Anne Deveson from *Chemistry a European Journal*.

After the dinner, guests will be able to view the posters and socialise in the Great Hall until midnight.

Carles **Bo** Exploring the PoCheMoN World with “in-silico” tools	**K04**
Marcella **Bonchio** Bio-inspired Nano-architectures for Artificial Photosynthesis	**K01**
Colette **Boskovic** Lanthanoid-Polyoxometalates: Single-Molecule Magnetism, Inelastic Neutron Scattering and Ab Initio Studies	**K05**
Emmanuel **Cadot** About Supramolecular Chemistry with Very Large Polyoxometalates	**K06**
Eugenio **Coronado** Magnetic polyoxometalates for quantum technologies	**K23**
Lee **Cronin** Mechanism of Self Assembly of Gigantic Inorganic Clusters	**K21**
R. John **Errington** New Insight, Further Questions: Targeted Non-Aqueous Polyoxometalate Synthesis.	**K12**
John **Fielden** Donor-Acceptor Organo-Imido POMs: New Materials for Photonics and Solar Energy Conversion	**K24**
José Ramon **Galan-Mascaros** Polyoxometalate composites for heterogeneous water oxidation catalysis	**K31**
Craig L. **Hill** Counter Cation Studies in New POM-based Materials	**K08**
Oxana A. **Kholdeeva** Aromatic oxidations with di-vanadium-substituted γ-Keggin polyoxotungstate: new reactions, mechanistic insights and immobilization approaches	**K16**
Walter G. **Klemperer** Why Do Highly-Charged Polyions with Univalent Counterions Form Spherical Shells – an Unanswered Question?	**K26**
Paul **Kögerler** Revisiting some polyoxometalate archetypes	**K29**
Ulrich **Kortz** Recent Developments in Polyoxopalladate Chemistry	**K10**
Yang-Guang **Li** Polyoxometalate-originated high efficient non-noble-metal electrocatalysts for hydrogen evolution reaction	**K03**
Pierre **Mialane** Using the Robustness of Polyoxometalates for the Elaboration of Materials with Properties Ranging from Magnetic to Optical	**K17**
Haralampos N. **Miras** Directed Self-Assembly, Electronic Modulation and Isomer “locking” in POM systems	**K28**
Ronny **Neumann** The Importance of Electron Transfer in Polyoxometalate-Catalysed Reactions: Photoelectrochemical Reduction of CO_2 and Electron-Transfer Oxidation of Benzene	**K15**

Pavel A. **Abramov** **C19**
From giant chalcoPOMs to giant polyoxoniobates

Beñat **Artetxe** **C03**
New Perspectives for Old Clusters: Anderson–Evans Anions as Building Blocks of Heterometallic 3d–4f POM Frameworks

Wassim **Ayass** **C09**
Introducing Thallium in Polyoxometalate Chemistry

Nuno A. G. **Bandeira** **C15**
Structural Changes of a Vanadium Polyoxoanion: A Mystery

Bassem S. **Bassil** **C04**
Lacunary Heteropolytungstates Stabilizing Polynuclear Magnetic 3d-Transition Metal Cores

Jorge J. **Carbó** **C13**
Computational modeling of polyoxometalate-protein interactions

Yan **Duan** **C25**
A decacobalt(II) cluster with triple-sandwich structure obtained by reductive hydrolysis of a pentacobalt(II/III), Weakley-type, polyoxometalate

Carlos **Giménez-Saiz** **C23**
Construction of larger polyoxometalates using the cubane-containing $[Co_4(OH)_3(H_2O)_6(PW_9O_{34})]^{4-}$ as a building block

Masooma **Ibrahim** **C22**
Nanometer-Size Heterometallic Polyoxometalate Clusters for Functional Applications

Natalya V. **Izarova** **C10**
Palladate/Tungstate Hybrids

Pawel J. **Kulesza** **C05**
Importance of Specific Metal-Polyoxometallate Interactions in Efficient Charge Propagation and Electro(photo)catalysis

Zhengguo **Lin** **C20**
Chiral Dodecanuclear Palladium(II)-Thio Cluster: Synthesis, Structure, and Formation Mechanism

De-Liang **Long** **C11**
Constructing high nuclearity polyoxotungstates with the aid of silver(I) counter-cation

Thi Kim Nga **Luong** **C14**
Detailed Mechanism of ATP Hydrolysis Promoted by a Binuclear Zr^{IV}-Substituted Keggin Polyoxometalate Elucidated by a Combination of ^{31}P, ^{31}P DOSY and ^{31}P EXSY NMR Spectroscopy

Hong Giang Thi **Ly** **C24**
Zr(IV)-Substituted Polyoxometalates as a novel class of artificial proteases: Catalytic and molecular interaction studies

Nataliya V. **Maksimchuk** **C12**
Mono- and di-titanium-substituted Lindqvist tungstates as catalysts for heterolytic activation of H_2O_2

Jun **Peng** **C29**
Preparation of a nanocomposite composed of polyoxometalates and cationized graphene for aqueous supercapacitors

Tânia Vanessa Oliveira **Pinto** Designing novel SiO_2@NH_2-PMo_{11}V based nanomaterials with reversible photo- and thermochromic properties	**C21**
Santiago **Reinoso** Thermo-Structural Studies in Vanadate–Metalorganic Hybrid Compounds: Dynamic vs. Robust Open-Framework Materials	**C16**
Soumyabrata **Roy** Decavanadate Based Hetero-metallic Inorganic-organic Hybrids as Highly Active Electro-catalysts for Hydrogen Evolution	**C02**
Laurent **Ruhlmann** Porphyrin-Polyoxometalate Electropolymers for the Photoelectrochemical Energy Conversion	**C01**
Roy E. **Schreiber** Colloids of POMs as a Mechanistic Step for Chemical Reactivity	**C06**
Zois **Syrgiannis** Polyoxometalate Nano Hair Clips: From Carbon Nanostructures recognition to applications	**C28**
Anne-Lucie **Teillout** The Wells-Dawson Polyoxotungstates: re-exploring their electrochemical behaviour in solution.	**C08**
Yizhan **Wang** Polyoxometalate-Protected Gold-Nanoparticle Building Units	**C27**
Jingli **Xie** STM Investigation of the Co-assembly Behaviour of POMs clusters with Host Molecule 1,3,5-tris(10-carboxydecyloxy)benzene (TCDB)	**C18**
Feng **Xu** Complex Assembly of $\{Cu_6\}$-Incorporated Icosametallic Clusters	**C07**
Weimin **Xuan** Self-Templating and *in-situ* Assembly of a Cubic Cluster-of Cluster Architectures based on a $\{Mo_{24}Fe_{12}\}$ Inorganic Macrocycle	**C26**
Panchao **Yin** X-ray and Neutron Scattering Study of the Formation of Core-Shell Type Polyoxometalates	**C30**
Qi **Zheng** Following the Reaction of Heteroanions inside a $\{W_{18}O_{56}\}$ Polyoxometalate Nanocage by NMR Spectroscopy and Mass Spectrometry	**C17**

Pavel A. **Abramov** Polyoxoniobates containing Noble Metals	**P01**
Wassim W. **Ayass** Introducing Thallium in Polyoxometalate Chemistry	**P02**
Amandine **Boulmier** Polyoxometalate Bisphosphonate Complexes: Synthesis, Structure and Activity on Tumor Cell Lines	**P23**
Biswarup **Chakraborty** Polyoxometalates complexes of α-Fe_2O_3 cores in water	**P24**
Bo **Chen** Ion pair tuned cyclic voltammetry behavior of Keggin polyoxometalate quaternary ammonium salts in organic solvents	**P25**
Mirjana B. **Čolović** The influence of synthesized polyoxometalates on acetylcholinesterase activity	**P26**
Pedro **de Oliveira** Polyoxometalate electro-oxidation of sulphur-containing molecules	**P03**
Chandan **Dey** Organic Photosensitizer attached Polyoxometalate as Catalyst for Reduction of CO_2	**P04**
Lan **Feng** Exploration of Synergy between Ruthenium Nanoparticles and Polyoxometalates for Biomass Conversion Catalysis	**P05**
Masaru **Fujibayashi** Understanding of formation process of $[Na(PhPO_3)_4(SO_3)_2Mo^{V}_4Mo^{VI}_{14}O_{49}]^{5-}$ characterized by ^{31}P-NMR	**P27**
Gal **Gan-Or** Polyoxometalates as capping ligands for water-soluble ZrO_2 nanoparticles	**P28**
Robin **Güttinger** Structural and magnetic investigations of a mononuclear 4f polyoxometalate family with single molecule magnet behaviour	**P21**
Natalya V. **Izarova** Iridium-Containing Polyoxometalates with Unique double Anderson-Evans Structure	**P06**
Thompson **Izuagie** Non-aqueous Synthesis and Electrochemical Behaviour of Post-Transition Metal Substituted Keggin Polyoxotungstates	**P07**
Danijela Z. **Krstić** The influence of synthesized polyoxotungstates on Na^+/K^+-ATPase activity	**P29**
Zhong Ling **Lang** DFT Study of Polyoxometalates on Gold Surfaces: from Structure to Catalysi	**P08**
Daniel **Lebbie** Polyoxometalates as Pincer Ligands?	**P09**
Edward **Lee** Robotics in POM discovery – incorporating automation	**P30**
Zhengguo **Lin** Chiral Dodecanuclear Palladium(II)-Thio Cluster: Synthesis, Structure, and Formation Mechanism	**P31**

Tian **Ma** Organoantimony-Containing Polyoxometalates and their Biological Activity	**P32**
Jagoba **Martín Caballero** Sequential Single–Crystal–to–Single–Crystal Transformations in a 3D Covalent Heptatungstate-based Hybrid with Permanent Porosity	**P10**
Mercè **Martin-Sabi** Synthesis of a Series of Tuneable Polyoxometalates for Water Oxidation	**P11**
Marcel P. **Merkel** Polyoxometalate-based Inorganic/Organic Hybrids	**P17**
Mhamad-Aly **Moussawi** Towards Stereoselectivity within mixed W/Mo Pentagaonal Building Units in Giant Polyoxometalates	**P33**
Magda **Pascual-Borràs** Computational insight into photochemical H_2 evolution by an iridium (III)-photosensitized polyoxotungstate	**P12**
Jun **Peng** Preparation of a nanocomposite composed of polyoxometalates and cationized graphene for aqueous supercapacitors	**P13**
Felix **Pfanschilling** Polyoxometalates for Redox Flow Batteries	**P14**
Jamie W. **Purcell** $[Mo_2O_2S_2]^{2+}$ as a Precursor to Chalcogen-infused Molecular Nano-Materials	**P34**
Soumyabrata **Roy** Decavanadate Based Hetero-metallic Inorganic-organic Hybrids as Highly Active Electrocatalysts for Hydrogen Evolution	**P15**
William **Salomon** POM-based materials as electrocatalysts for proton and NOx reduction	**P16**
Stefano Artin **Serapian** That organic extra something: *in silico* studies on two remarkable organic-polyoxometalate hybrids	**P18**
Shan **She** Organically-Derivatized Polyoxometalates with Enhanced Anticancer Activity	**P35**
Maria **Stuckart** Regular Pattering of Polyoxometalates on Surfaces	**P19**
Zelin **Wang**	**P36**
Adam Scott **Weingarten** Supramolecular Organization of Graphene-anchored Photosynthetic Nano-arrays	**P20**
Lin **Xu** A novel heteropoly blue based on Dawson-type tungstogermanates: Crystal Structures and Magnetic Properties	**P22**

Detailed Conference Programme

Sunday 10th July

11:00 – 13:00		Registration
13:00 – 13:30		Opening Remarks

Session Chair **R. J. Errington**

13:30 – 14:00	**K01**	Marcella **Bonchio**, *University of Padova* Bio-inspired Nano-architectures for Artificial Photosynthesis
14:00 – 14:30	**K02**	Josep M. **Poblet,** *URV Tarragona* Catalytic reactions involving functionalized polyoxometalates
14:30 – 14:45	**C01**	Laurent **Ruhlmann,** *Université de Strasbourg* Porphyrin-Polyoxometalate Electropolymers for the Photoelectrochemical Energy Conversion
14:45 – 15:00	**C02**	Soumyabrata **Roy,** *Jawaharlal Nehru Centre for Advanced Scientific Research* Decavanadate Based Hetero-metallic Inorganic-organic Hybrids as Highly Active Electro-catalysts for Hydrogen Evolution
15:00 – 15:30	**K03**	Yang-Guang **Li,** *Northeast Normal University* Polyoxometalate-originated high efficient non-noble-metal electrocatalysts for hydrogen evolution reaction
15:30 – 16:00		Coffee Break

Session Chair **J.-M. Poblet**

16:00 – 16:30	**K04**	Carles **Bo,** *ICIQ Tarragona* Exploring the PoCheMoN World with “in-silico” tools
16:30 – 17:00	**K05**	Colette **Boskovic,** *University of Melbourne* Lanthanoid-Polyoxometalates: Single-Molecule Magnetism, Inelastic Neutron Scattering and Ab Initio Studies
17:00 – 17:15	**C03**	Beñat **Artetxe,** *Universidad del País Vasco* New Perspectives for Old Clusters: Anderson–Evans Anions as Building Blocks of Heterometallic 3d–4f POM Frameworks
17:15 – 17:30	**C04**	Bassem S. **Bassil,** *Jacobs University* Lacunary Heteropolytungstates Stabilizing Polynuclear Magnetic 3d-Transition Metal Cores
17:30 – 18:00	**K06**	Emmanuel **Cadot,** *Institut Lavoisier, Université Versailles* About Supramolecular Chemistry with Very Large Polyoxometalates
18:00 – 18:30	**K07**	Helena I. S. **Nogueira,** *University of Aveiro* Raman imaging and SERS studies on polyoxometalates and its nanocomposites

Monday 11th July

Session Chair **M. Bonchio**

9:00 – 9:30	**K08**	Craig L. **Hill,** *Emory University* Counter Cation Studies in New POM-based Materials
9:30 – 9:45	**C05**	Pawel J. **Kulesza,** *University of Warsaw* Importance of Specific Metal-Polyoxometallate Interactions in Efficient Charge Propagation and Electro(photo)catalysis
9:45 – 10:00	**C06**	Roy E. **Schreiber,** *Weizmann Institute of Science* Colloids of POMs as a Mechanistic Step for Chemical Reactivity
10:00 – 10:30	**K09**	Sayaka **Uchida,** *The University of Tokyo* Reduction-Induced Uptake of Alkali Metal Cations by Porous Ionic Crystals based on Polyoxomolybdates
10:30 – 11:00		Coffee Break

Session Chair **E. Cadot**

11:00 – 11:30	**K10**	Ulrich **Kortz,** *Jacobs University* Recent Developments in Polyoxopalladate Chemistry
11:30 – 11:45	**C07**	Feng **Xu,** *Hunan University* Complex Assembly of $\{Cu_6\}$-Incorporated Icosametallic Clusters
11:45 – 12:00	**C08**	Anne-Lucie **Teillout,** *Université Paris-Sud* The Wells-Dawson Polyoxotungstates: re-exploring their electrochemical behaviour in solution
12:00 – 12:30	**K11**	Maxim N. **Sokolov,** *Nikolaev Institute of Inorganic Chemistry* New polyoxometalate complexes of noble metals

12:30 – 13:30 Lunch Break

Session Chair **A. Proust**

13:30 – 14:00	**K12**	R. John **Errington,** *Newcastle University* New Insight, Further Questions: Targeted Non-Aqueous Polyoxometalate Synthesis
14:00 – 14:30	**K13**	Yongge **Wei,** *Tsinghua University* Chemical Modification of Polyoxometalates and their Applications
14:30 – 14:45	**C09**	Wassim **Ayass,** *Jacobs University* Introducing Thallium in Polyoxometalate Chemistry
14:45 – 15:00	**C10**	Natalya V. **Izarova,** *Peter Grünberg Institute* Palladate/Tungstate Hybrids
15:00 – 15:30	**K14**	Chris **Ritchie,** *University of Melbourne* Microwave assisted synthesis, structural isomers and more…

15:30 – 16:00 Coffee Break

Session Chair **Y.-G. Li**

16:00 – 16:30	**K15**	Ronny **Neumann,** *Weizmann Institute* The Importance of Electron Transfer in Polyoxometalate-Catalysed Reactions: Photoelectrochemical Reduction of CO_2 and Electron-Transfer Oxidation of Benzene
16:30 – 17:00	**K16**	Oxana A. **Kholdeeva,** *Boreskov Institute of Catalysis* Aromatic oxidations with di-vanadium-substituted γ-Keggin polyoxotungstate: new reactions, mechanistic insights and immobilization approaches
17:00 – 17:15	**C11**	De-Liang **Long,** *University of Glasgow* Constructing high nuclearity polyoxotungstates with the aid of silver(I) counter-cation
17:15 – 17:30	**C12**	Nataliya V. **Maksimchuk,** *Boreskov Institute of Catalysis* Mono- and di-titanium-substituted Lindqvist tungstates as catalysts for heterolytic activation of H_2O_2
17:30 – 18:00	**K17**	Pierre **Mialane,** *Université de Versailles* Using the Robustness of Polyoxometalates for the Elaboration of Materials with Properties Ranging from Magnetic to Optical
18:00 – 18:30	**K18**	Ryo **Tsunashima** , *Yamaguchi University* Mixed-valence Polyoxometalate; a molecular nanoparticle for macroscopic electrical properties

Tuesday, 12th July

Session Chair **L. Cronin**

9:00 – 9:30	**K19**	Tatjana N. **Parac-Vogt,** *KU Leuven* Metal-substituted polyoxometallates as artificial nucleases
9:30 – 9:45	**C13**	Jorge J. **Carbó,** *Universitat Rovira i Virgili, Tarragona* Computational modeling of polyoxometalate-protein interactions

9:45 – 10:00	**C14**	Thi Kim Nga **Luong,** *KU Leuven* Detailed Mechanism of ATP Hydrolysis Promoted by a Binuclear Zr^{IV}-Substituted Keggin Polyoxometalate Elucidated by a Combination of ^{31}P, ^{31}P DOSY and ^{31}P EXSY NMR Spectroscopy
10:00 – 10:30	**K20**	Lixin **Wu,** *Jilin University* Induced Chirality and Chirality Transfer in Polyoxometalate Systems
10:30 – 11:00		Coffee Break

Session Chair **L. Wu**

11:00 – 11:30	**K21**	Lee **Cronin,** *University of Glasgow* Mechanism of Self Assembly of Gigantic Inorganic Clusters
11:30 – 11:45	**C15**	Nuno A. G. **Bandeira,** *ICIQ, Barcelona Institute of Science and Technology* Structural Changes of a Vanadium Polyoxoanion: A Mystery
11:45 – 12:00	**C16**	Santiago **Reinoso,** *Universidad del País Vasco* Thermo-Structural Studies in Vanadate–Metalorganic Hybrid Compounds: Dynamic vs. Robust Open-Framework Materials
12:00 – 12:30	**K22**	Yu-Fei **Song,** *Beijing University of Chemical Technology* Polyoxometalate-functionalized nanocarbon as energy materials
12:30 – 13:30		Lunch Break

Session Chair **U. Kortz**

13:30 – 14:00	**K23**	Eugenio **Coronado,** *ICMol, University of Valencia* Magnetic polyoxometalates for quantum technologies
14:00 – 14:30	**K24**	John **Fielden,** *University of East Anglia* Donor-Acceptor Organo-Imido POMs: New Materials for Photonics and Solar Energy Conversion
14:30 – 14:45	**C17**	Qi **Zheng,** *University of Glasgow* Following the Reaction of Heteroanions inside a $\{W_{18}O_{56}\}$ Polyoxometalate Nanocage by NMR Spectroscopy and Mass Spectrometry
14:45 – 15:00	**C18**	Jingli **Xie,** *Jiaxing University* STM Investigation of the Co-assembly Behaviour of POMs clusters with Host Molecule 1,3,5-tris(10-carboxydecyloxy)benzene (TCDB)
15:00 – 15:30	**K25**	Dominique **Vuillaume,** *CNRS, Lille* Optical and electrical properties of molecular junctions and networks
15:30 – 16:00		Coffee Break

Session Chair **I. Weinstock**

16:00 – 16:30	**K26**	Walter G. **Klemperer,** *University of Illinois* Why Do Highly-Charged Polyions with Univalent Counterions Form Spherical Shells – an Unanswered Question?
16:30 – 17:00	**K27**	Sebastian **Polarz,** *University of Konstanz* Organic-Inorganic Surfactants: Hybrids with Polyoxometalate Heads and Beyond
17:00 – 17:15	**C19**	Pavel A. **Abramov,** *Nikolaev Institute of Inorganic Chemistry* From giant chalcoPOMs to giant polyoxoniobates
17:15 – 17:30	**C20**	Zhengguo **Lin,** *Jacobs University* Chiral Dodecanuclear Palladium(II)-Thio Cluster: Synthesis, Structure, and Formation Mechanism
17:30 – 18:00	**K28**	Haralampos N. **Miras,** *University of Glasgow* Directed Self-Assembly, Electronic Modulation and Isomer “locking” in POM systems
18:00 – 18:30	**K29**	Paul **Kögerler,** *RWTH Aachen* Revisiting some polyoxometalate archetypes

Wednesday, 13th July

Session Chair **E. Coronado**

9:00 – 9:30	**K30**	Greta R. **Patzke,** *University of Zurich* Water Oxidation Catalysis with Oxoclusters: From POMs to Cubanes
9:30 – 9:45	**C21**	Tânia Vanessa Oliveira **Pinto,** *Universidade do Porto* Designing novel SiO_2@NH_2-$PMo_{11}V$ based nanomaterials with reversible photo- and thermochromic properties
9:45 – 10:00	**C22**	Masooma **Ibrahim,** *Karlsruhe Institute of Technology (KIT) Institute of Nanotechnology (INT)* Nanometer-Size Heterometallic Polyoxometalate Clusters for Functional Applications
10:00 – 10:30	**K31**	José Ramon **Galan-Mascaros,** *ICIQ Tarragona* Polyoxometalate composites for heterogeneous water oxidation catalysis
10:30 – 11:00		Coffee Break

Session Chair **C. Streb**

11:00 – 11:05	**S01**	Svetlana **Baca**, *Academy of Sciences of Moldova* Homo- and heterometallic Fe/4f based assemblies with enhanced magnetic properties
11:05 – 11:10	**S02**	Thompson **Izuagie**, *Newcastle University, UK* Solution Electrochemistry and Electrocatalytic Studies on a range of Mono-Substituted Heterometallic Polyoxometalates
11:10 – 11:15	**S03**	Mercè **Martin-Sabi**, *University of Glasgow, UK* Synthesis of a Series of Tuneable Polyoxometalates for Water Oxidation
11:15 – 11:20	**S04**	Dolores **Melgar**, *ICIQ, Tarragona* Polyoxometalate as Cryptate for Apolar Ions
11:20 – 11:25	**S05**	Magda **Pascual-Borràs**, *ICIQ, Tarragona* Mechanistic studies on heterometallic Lindqvist and Keggin-type Polyoxometalates
11:25 – 11:30	**S06**	Joaquin **Soriano-Lopez**, *ICIQ, Tarragona* Heterogeneous Light-Driven Water Oxidation Catalysis with Cobalt Containing Polyoxometalates
11:30 – 11:45	**C23**	Carlos **Giménez-Saiz,** *ICMol, University of Valencia* Construction of larger polyoxometalates using the cubane-containing $[Co_4(OH)_3(H_2O)_6(PW_9O_{34})]^{4-}$ as a building block
11:45 – 12:00	**C24**	Hong Giang Thi **Ly,** *KU Leuven* Zr(IV)-Substituted Polyoxometalates as a novel class of artificial proteases: Catalytic and molecular interaction studies
12:00 – 12:15	**C25**	Yan **Duan,** *ICMol, University of Valencia* A decacobalt(II) cluster with triple-sandwich structure obtained by reductive hydrolysis of a pentacobalt(II/III), Weakley-type, polyoxometalate
12:15 – 12:30	**C26**	Weimin **Xuan,** *University of Glasgow* Self-Templating and *in-situ* Assembly of a Cubic Cluster-of Cluster Architectures based on a $\{Mo_{24}Fe_{12}\}$ Inorganic Macrocycle
12:30 – 13:00		**Flash Presentations – poster 'pitches'**
13.30 – 17:30		**Historical walk**
16:00 – 18:00		**Put up posters**
18:00 – 19:00		**Reception and poster viewing**
19:00 – 21:00		**Conference Dinner**
20.30		**Poster prize presentations**
21:00 – 00:00		**Social & poster viewing**

Thursday, 15th July

Session Chair **R. Neumann**

9:00 – 9:30	K32	Anna **Proust,** *Université Pierre et Marie Curie* Polyoxometalates as functional building blocks
9:30 – 9:45	C27	Yizhan **Wang,** *Ben-Gurion University of the Negev* Polyoxometalate-Protected Gold-Nanoparticle Building Units
9:45 – 10:00	C28	Zois **Syrgiannis,** *ITM-CNR, Padua* Polyoxometalate Nano Hair Clips: From Carbon Nanostructures recognition to applications
10:00 – 10:30	K33	Ira **Weinstock,** *Ben-Gurion University* Polyoxometalate complexes of metal-oxide nanocrystals
10:30 – 11:00		Coffee Break

Session Chair **P. Kögerler**

11:00 – 11:15	C29	Jun **Peng,** *Northeast of Normal University* Preparation of a nanocomposite composed of polyoxometalates and cationized graphene for aqueous supercapacitors
11:15 – 11:30	C30	Panchao **Yin,** *Oak Ridge National Laboratory* X-ray and Neutron Scattering Study of the Formation of Core-Shell Type Polyoxometalates
11:30 – 12:00	K34	Carsten **Streb,** *Ulm University* Molecular Metal Chalcogenides for Energy Conversion and Storage
12:00 – 12:30		Closing Remarks
13:00 – 15:00		**COST Action CM1203 PoCheMoN MC meeting**

Bio-inspired Nano-architectures for Artificial Photosynthesis

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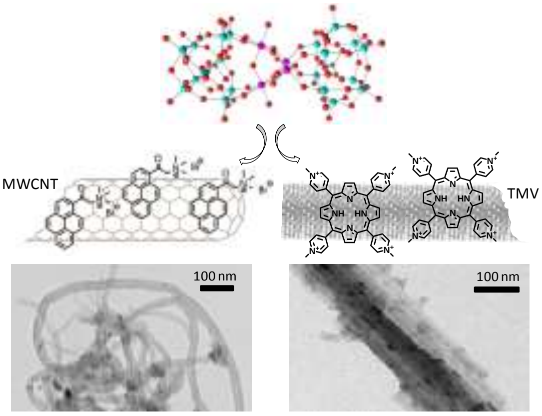
Abstract

The perfect machinery of Natural Photosynthesis, powering our daily life with solar energy, is shaped by a modular network of photocomplexes, where molecular/nano-range order and distances are precisely tuned on membrane-bound compartments. Along these guidelines, the current frontier of Artificial Photosynthesis looks at a multi-component, interconnected system, where the cross-talk of photo-active and catalytic building blocks is pivotal to implement function and optimization/repair strategies. In this *scenario*, the use of biogenic nano-templates has a major appeal, considering their renewable origin, the high density of surface reactive sites, and site-specific synthetic protocols available for their derivatization. These biogenic scaffolds offer a unique alternative to synthetic nano-platforms for the assembly of functional molecules and materials. Different synthetic strategies are herein highlighted depending on the building blocks and with particular emphasis on the molecular design of viral-templated nano-interfaces holding a great potential for the dream-goal of artificial photosynthesis (Figure 1).



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Catalytic reactions involving functionalized polyoxometalates

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Abstract

In this communication, we report some recent results of our group concerning the theoretical analysis of the role that functionalized polyoxometalates play in reactions such as production of H_2, CO_2 reduction and water splitting processes when the reaction is activated electrochemically or photocatalytically. One of the abilities of polyoxometalates is that they can store several electrons with modest difference in potentials between successive reduction steps. Then, polyoxometalates are attractive candidates to act as photo-accumulators. We will show several examples where functionalized polyoxotungstates act as a reservoir of electrons that may use the electrons to catalyze different reactions. We will also describe the mechanism of water oxidation catalyzed by Co containing polyoxometalates.

Polyoxometalate-originated high efficient non-noble-metal electrocatalysts for hydrogen evolution reaction

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Abstract

The hydrogen evolution reaction (HER) via an electrocatalytic water-splitting method is considered as a promising approach for the exploration of hydrogen energy.[1] A key problem of this method is seeking highly active, stable and cheap electrocatalysts that can substitute the currently best but the most expensive Pt electrocatalyst. In this research field, the molybdenum & tungsten-based electrocatalysts have exhibited excellent HER performance in contrast to Pt. Considering that the nanoscale polyoxometalates (POMs) contain abundant molybdenum & tungsten metal centers, POMs may be used as ideal precursors to design and prepare new non-noble-metal electrocatalysts for HER. During the preparation, POMs will be employed as a molecular assembly platform to precisely tune various metal components and structural features. Furthermore, the combination of POMs with a series of organic dopants (C, N, P, S etc), dispersants and carrier materials will lead to various assemblies that can disperse POM units at the molecular level (Fig. 1),[2] which will be annealed at limited range so as to obtain new type of nanoscale low-valent metal (Mo/W) oxides, metal carbides, phosphide, and sulfide electrocatalytic materials for HER. Herein, we will introduce some of our recent research results in this project.[3]

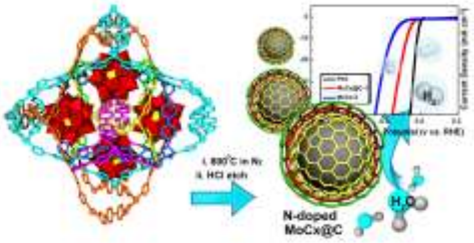

Fig. 1 N-doped MoCx@C nanoscale electrocatalysts prepared from a POM-based MOFs

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Exploring the PoCheMoN World with “in-silico” tools

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Abstract

During the last five years we have been exploring computationally a variety of chemical phenomena, namely the electronic structure, reactivity and properties of Keplerates, aggregation and ion-pairing of lacunary and hybrid polyoxometalates, structure and stability of polyoxocations, etc.

This talk will summarize the main results obtained within the framework of the PoCheMoN action, and will present results of recent studies.

Lanthanoid-Polyoxometalates: Single-Molecule Magnetism, Inelastic Neutron Scattering and *Ab Initio* Studies

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Abstract

The structural rigidity and large negative charge of polyoxometalates (POMs) confer on lanthanoid ions with POM ligands a very different local coordination environment to that available with organic ligands. The study of POM-supported lanthanoid-single molecule magnets (Ln-SMMs) can thus afford new insights into the effect of lanthanoid coordination on Ln-SMM properties,[1] which is of relevance for future applications in quantum computing and molecular spintronics.

We have applied a concerted experimental and theoretical approach to investigate the $[Ln(W_5O_{18})_2]^{9-}$ family of Ln-SMMs.[2] Inelastic neutron scattering (INS), magnetochemical and *ab initio* studies have revealed the sensitivity of the electronic structure of the ground and excited states of $[Tb(W_5O_{18})_2]^{9-}$ to small structural distortions from axial symmetry, thus highlighting the subtle relationship between molecular geometry and magnetic properties.[3]

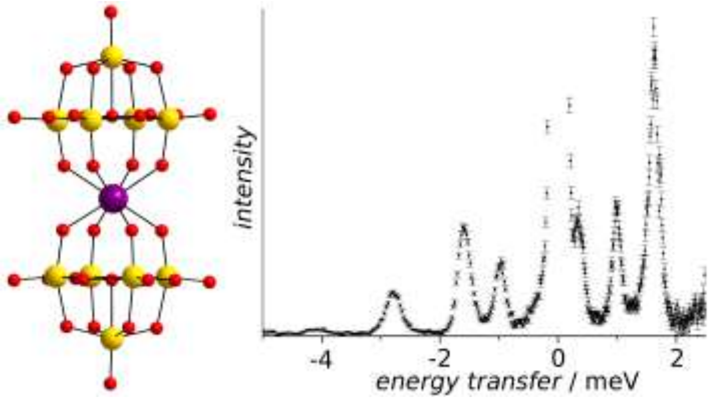

Figure 1. $[Ln(W_5O_{18})_2]^{9-}$: (left) structure & (right) 30 K INS spectrum for Ln = Tb.[3]

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About Supramolecular Chemistry with Very Large Polyoxometalates

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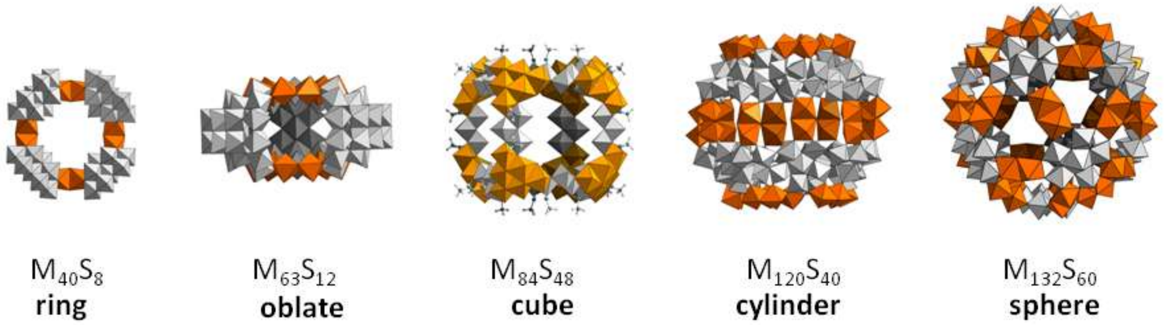
Abstract

Synthetic approaches for the formation of the literally “polyoxo**thio**metalate” compounds (or ChalcoPOMs) with a special emphasis on the unique reactivity of the preformed sulphur-containing cationic Mo-S building block toward polyoxometalate units.[1] Such a simple chemical system based on chemical and structural complementarities between constitutive modular units has allowed producing a series of relevant very large hollow clusters with unrivalled structural arrangements, like ring, cylinder, cubic boxe or sphere (see Figure 1). [3,4] Specific reaction parameters and considerations will be discussed showing that a deliberate *pure* inorganic supramolecular chemistry based on weak interactions, flexibility and dynamics is achievable with polyoxometalates. Furthermore solution investigations revealed striking supramolecular properties involving related events such as surface adsorption, transfer processes and confined situations.[5]



$M_{40}S_8$ **ring** | $M_{63}S_{12}$ **oblate** | $M_{84}S_{48}$ **cube** | $M_{120}S_{40}$ **cylinder** | $M_{132}S_{60}$ **sphere**

Figure 1: Molecular topologies resulting from polyoxometalate units (grey) and $\{Mo_2O_2E_2\}$ linker (orange)

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Raman imaging and SERS studies on polyoxometalates and its nanocomposites

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Abstract

The current developments of techniques such as Raman imaging, through high resolution Raman mapping with short measurement times, have brought a new look on composites and its applications. Using Raman imaging, composite particles can now be evaluated from its Raman signal over a specific surface area with spatial resolution within the sub-micrometer range. Such an image can show either the chemical heterogeneity or a specific response such as SERS (surface-enhanced Raman scattering) activity[1] or a labeling process[2] (Figure 1).

SERS also brings new insights in the studies on the molybdenum blue polyoxometalates such as the hedgehog-shaped {Mo_{368}} cluster in which the high number of delocalized electrons allows the measurement of the SERS spectrum.[3]

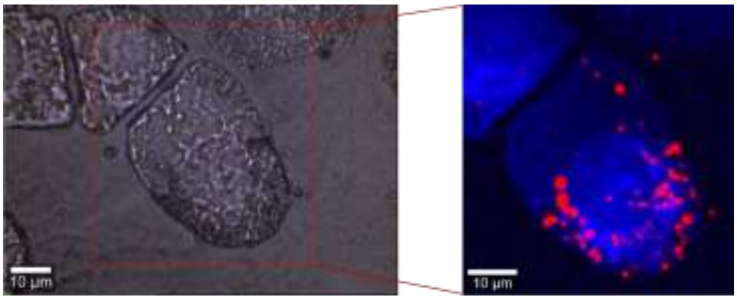

Figure 1 – Bio-labeling of human bladder cancer cells using lanthanopolyoxotungstate/silica nanocomposites: optical image (left) and Raman imaging of the selected area (right).

Acknowledgements: Thanks are due to Fundação para a Ciência e a Tecnologia (FCT, Portugal), CICECO - Aveiro Institute of Materials and COST CM1203 action for funding.

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Counter Cation Studies in New POM-based Materials

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Abstract

Polyoxometalate counter cation effects will be discussed in 3 new types of POMs or POM-based materials we are currently developing. The first type are polyniobate polymers that catalyze the rapid hydrolysis of various esters in the liquid and gas phases by a general base mechanism based on several kinetic experiments and computational studies.[1] The second type are esterified polyvanadate-based polymers that form barriers to penetration by various dangerous compounds and catalyze their degradation by three mechanisms based on the components of the polymer. A new form of these polymers has just been developed that is an extremely reactive hydrolysis catalyst. The third type are particular polyvanadates with unusual charge profiles that are potent antitumor agents. They appear to act by a novel mechanism.

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Reduction-Induced Uptake of Alkali Metal Cations by Porous Ionic Crystals based on Polyoxomolybdates

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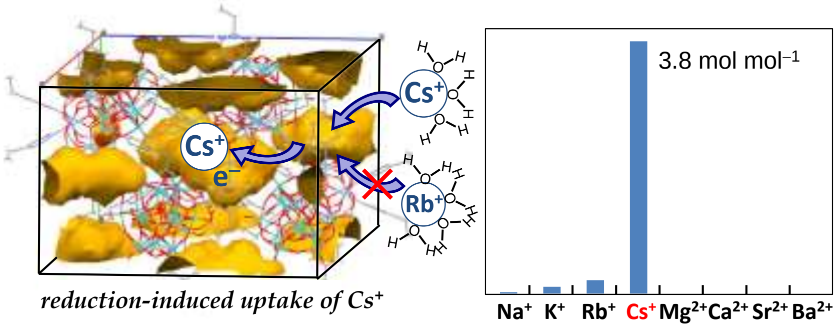
Abstract



Selective uptake of alkali metal cations from aqueous solutions has been an important topic in chemistry relevant to material synthesis as well as purification and separation. Especially, selective uptake of Cs$^+$ is important because it is expensive and contained in radioactive wastes. Zeolites, prussian blue, and layered compounds have been researched and applied as Cs$^+$ adsorbents. However, these materials adsorb Rb$^+$ as well as Cs$^+$, and an adsorbent with high selectivity toward Cs$^+$ has not yet been reported. In this work, an ionic crystal $(\mathrm{etpyH})_2[\mathrm{Cr_3O(OOCH)_6(etpy)_3}]_2[\alpha\text{-}\mathrm{SiMo_{12}O_{40}}]\cdot 3\mathrm{H_2O}$ (etpy = 4-ethylpyridine, etpyH$^+$ = 4-ethylpyridinium ion) with closed pores was synthesized.[1] The compound incorporated up to 3.8 mol mol^{-1} of Cs$^+$ via cation-exchange with etpyH$^+$ and reduction of silicododecamolybdate $[\alpha\text{-SiMo(VI)12O40}]^{4-}$ to $[\alpha\text{-}\mathrm{SiMo(V)}_n\mathrm{Mo(VI)}_{12-n}\mathrm{O}_{40}]^{(4+n)-}$ with ascorbic acid. Other alkali metal and alkaline earth metal cations were almost completely excluded (< 0.2 mol mol^{-1}). The high selectivity towards Cs$^+$ is due to the existence of closed pores instead of open channels. In addition, flexibility of the crystal lattice caused by isotropic and long-range Coulomb interactions among the constituent ions, may have contributed to the diffusion of Cs$^+$ between the closed pores.

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Recent Developments in Polyoxopalladate Chemistry

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The area of polyoxo-noble-metalates comprising exclusively d^8 metal centers such as Pd^{II} [1a] and Au^{III} [1b] was pioneered in 2008 and 2010, respectively, and has developed rapidly ever since. This is not unexpected, considering that this class of compounds exhibits fundamentally novel structural and compositional features, being based solely on square-planar building blocks, resulting in interesting properties and potential applications.[2] Polyoxopalladates(II) represent the largest subclass in the polyoxo-noble-metalate family. In terms of structural types, the symmetrical 12-palladate nanocube $\{Pd_{12}\}$ and the 15-palladate nanostar $\{Pd_{15}\}$ are the most abundant. Especially for the $\{Pd_{12}\}$ structure type, many derivatives containing various (*s*, *p*, *d*, and *f*-block) central cationic guest ions M^{n+} and different capping groups L are known nowadays, forming a very large family of $\{MPd_{12}L_8\}$.[2] Recently we reported on the 'open-nanocube' structure type {open-Pd_{12}},[3] Now we have succeeded in systematically derivatizing this {open-Pd_{12}} structure type by introducing new types of external ligands, resulting in compounds with unprecedented properties. These and other related results on polyoxopalladates will be presented here.

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New polyoxometalate complexes of noble metals

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Abstract

New hybrid POMs based on Lindqvist-type hexametalates $[M_6O_{19}]^{8-}$ (M = Nb, Ta) and organometallic fragments $\{Cp^*Rh\}^{2+}$ and $\{Cp^*Ir\}^{2+}$ have been isolated. $K_4[(Cp^*Rh)_2Nb_6O_{19}]\cdot 20H_2O$ and $Cs_4[(Cp^*Rh)_2Ta_6O_{19}]\cdot 18H_2O$ were obtained from solutions with $\{Cp^*Rh\}:[M_6O_{19}]^{8-}$ stoichiometry 2:1. Reaction of the hexametalates with $[Cp^*IrCl_2]_2$ in $[M_6O_{19}]^{8-}/\{Cp^*Ir\}^{2+}$ 1:2 molar ratio gave $A_4[\{Cp^*Ir\}_2M_6O_{19}]\cdot xH_2O$ (A = Na, M = Nb, x = 22; A = K, M = Nb, x = 22; A = Na, M = Ta, x = 24). When $[M_6O_{19}]^{8-}/\{Cp^*Ir\}^{2+}$ were reacted in 1:1 molar ratio, Nb and Ta behave in a different way. For M = Nb, the product was an oxo-bridged dimer with linear Nb-O-Nb central bridge, $[\{Cp^*IrNb_6O_{18}\}_2(\mu_2\text{-}O)]^{10-}$. For M = Ta only monomeric $[\{Cp^*Ir\}Ta_6O_{19}]^{6-}$ was detected. Solution behavior of new complexes was studied with NMR and ESI-MS techniques. CV experiments demonstrate efficient electrocatalytic water oxidation catalyzed by $[\{Cp^*Ir\}_2Nb_6O_{19}]^{4-}$.

Reaction of siliconiobate $K_{10}[Nb_2O_2][SiNb_{12}O_{40}]\cdot 16H_2O$ with $[(C_6H_6)RuCl_2]_2$ gives $[\{(C_6H_6)Ru\}_4SiNb_{12}O_{40}]^{8-}$, which contains Keggin-type $[SiNb_{12}O_{40}]^{16-}$ with four coordinated organometallic $\{(C_6H_6)Ru\}^{2+}$ units. $[VNb_{12}O_{40}]^{15-}$ behaves similarly.

Reactivities of $(Bu_4N)_4[PW_{11}O_{39}(Os^{VI}N)]$ and $(Bu_4N)_7[\alpha_2\text{-}P_2W_{17}O_{61}(Os^{VI}N)]$ have been investigated. Cyclic voltammetry shows accessibility of the Os^{VII} state upon oxidation of the $\{OsN\}^{3+}$ complexes. The nitride ligand can be removed with azide in CH_3CN with the formation of $[PW_{11}O_{39}(Os^{III}CH_3CN)]^{4-}$ and $[\alpha_2\text{-}P_2W_{17}O_{61}(Os^{III}CH_3CN)]^{7-}$ thus making available POMs with exchangeable ligand at the Os site. Related chemistry will be discussed.

This work was supported by Russian Scientific Foundation grant No. 14-13-00645

New Insight, Further Questions: Targeted Non-Aqueous Polyoxometalate Synthesis.

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Abstract

This talk will provide a brief overview of two strands of our research into non-aqueous polyoxometalate (POM) synthesis and present some recent results. Reactive $\{TiW_5\}$ and $\{SnW_5\}$ heterometallic Lindqvist-type polyoxometalates (POMs), prepared by hydrolytic aggregation from metal alkoxides,[1] have been used to probe the nature of protonolysis and protonation reactions. The effect of metal substitution on electronic properties and reaction rates has been assessed through systematic spectroscopic studies.[2] Recent results hint at new ways to use POMs as 'non-innocent' inorganic ligands to create molecular models for heterogeneous metal oxide catalysts raising the question – 'is it possible to design POMs for use as pincer ligands?'.

Our efforts to access different redox states of the $\{PMo_{12}O_{40}\}$ core Keggin unit through rational chemical reduction have resulted in a range of electron-rich, capped species.[3] The effects of varying the reaction conditions, the extension of the methodology to other POM structures and implications for the design of molecular spin qubits will be discussed.

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Chemical Modification of Polyoxometalates and their Applications

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Abstract

Recent development of the chemistry of organically-derivatized polyoxometalates (POMs) including organoimido and alkoxo derivatives of POMs in our group will be presented. Some important applications such as catalysis will also be introduced

Microwave assisted synthesis, structural isomers and more…

C. Ritchie,***** S. Spillane, R. Sharma, A. Zavras, A. Ohlin, L. Goerigk, S. P. Best,
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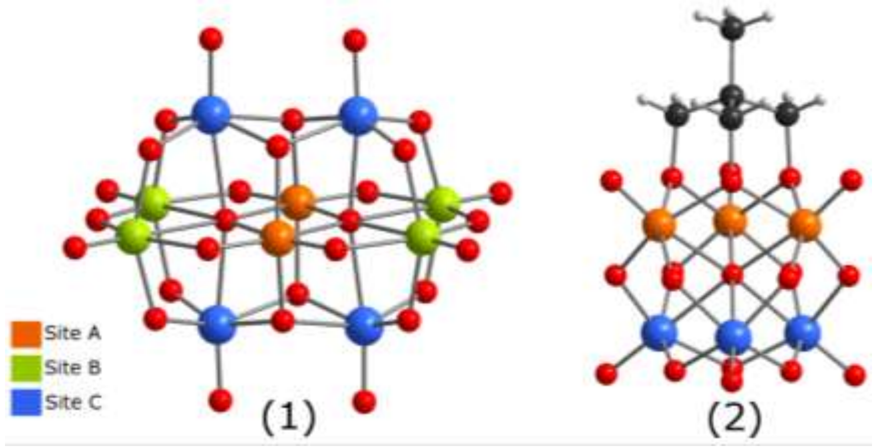
Abstract

Over the years numerous synthetic approaches have been tried and tested in search of heterometallates with specific atomic ratios and structural features. Here we report the initial findings of our non-aqueous microwave assisted strategy including evidence for the controllable disassembly, reassembly and fusion of common polyanions to yield novel heteropolymolybdates.[1,2] The structural and compositional features of these polyanions will be discussed, including the sorting of their structural isomers via experimental and theoretical approaches.



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K15

The Importance of Electron Transfer in Polyoxometalate-Catalysed Reactions: Photoelectrochemical Reduction of CO_2 and Electron-Transfer Oxidation of Benzene.

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Abstract

Two very different examples will given on the Importance of electron transfer in polyoxometalate catalyzed reactions. In the first example we discuss the photochemical reduction of CO_2 to CO that requires two electrons and two protons that are usually derived from sacrificial amine donors. In a hybrid complex that combines an acidic polyoxometalate, $H_3PW_{12}O_{40}$, as an electron and proton donor/acceptor or “electron shuttle” with a new di-rhenium molecular catalyst with a basic appendage we show a cascade of transformations, where (1) the polyoxometalate is electrochemically reduced at low potential, only 1.3 V versus Ag/Ag^+, and (2) visible light, 60 W tungsten lamp, is used to transfer electrons from the polyoxometalate to the di-rhenium CO_2 photoreduction catalyst active for the selective reduction of CO_2 to CO. The transformation proceeds via visible light excitation of the electrochemically reduced $H_3PW_{12}O_{40}$ that leads to electron transfer to the Re catalyst. This research is a key step for future photoelectrochemical CO_2 reductions that can be carried out on photovoltaic cells using earth abundant catalysts combining a water splitting reaction as the electron/proton source.

In the second example, we demonstrate that benzene can be oxidized by one electron using the $H_5PV_2Mo_{10}O_{40}$ polyoxometalate in sulfuric acid as an electron acceptor. UV-vis and low and high field EPR experiments will be presented that substantiates the formation and stabilization of a benzene cation radical. Upon heating the solution under O_2 phenol is formed. The research will also be discussed in the context off a novel pathway for the aerobic oxidation of benzene to phenol.

Aromatic oxidations with di-vanadium-substituted γ-Keggin polyoxotungstate: new reactions, mechanistic insights and immobilization approaches

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Abstract

The insertion of oxygen atom into aromatic nucleus is one of the most difficult transformations in the organic synthesis. While many polyoxometalates (POM) catalyze heterolytic activation of H_2O_2 and oxygen transfer to alkenes and thioethers, thus far only one POM, i.e. $(Bu_4N)_4[\gamma\text{-}PW_{10}O_{38}V_2(\mu\text{-}O)(\mu\text{-}OH)]$ (**I**), is known as an effective catalyst for aromatic hydroxylation [1,2]. This unique POM turned out a highly active and selective catalyst for oxidation of alkylphenols [3] and alkoxyarenes [4] to *p*-benzoquinones. The presence of acid co-catalyst is required for the oxidation of alkyl- and alkoxyarenes. Alternatively, a highly protonated form, $(Bu_4N)_{3.5}H_{0.5}[\gamma\text{-}PW_{10}O_{38}V_2(\mu\text{-}O)(\mu\text{-}OH)]$, can be prepared and used as the single catalyst [4].

Mechanistic features of the H_2O_2 activation by **I** toward arene oxygenation were studied using both experimental and theoretical methods. Product, spectroscopic (^{31}P and ^{51}V NMR), kinetic, and computational studies on pseudocumene hydroxylation implicated a mechanism of electrophilic oxygen atom transfer from a peroxo complex, $(Bu_4N)_3[\gamma\text{-}PW_{10}O_{38}V_2(O_2)]$, to the aromatic ring via arene oxide intermediate. A less sterically hindered hydroperoxo complex, $(Bu_4N)_3[\gamma\text{-}PW_{10}O_{38}V_2(\mu\text{-}O)(\mu\text{-}OOH)]$, is most likely involved in the oxidation of alkylphenols.

Various approaches to immobilization of **I** were explored. Nitrogen-doped carbon nanotubes have been identified as supports that ensure strong adsorption and molecular dispersion of **I** with retention of its structure and composition, leading to highly active, selective, truly heterogeneous, and recyclable catalysts.

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[4] O. V. Zalomaeva, V. Yu. Evtushok, O. A. Kholdeeva, *Adv. Synth. Catal*., submitted.

K17

Using the Robustness of Polyoxometalates for the Elaboration of Materials with Properties Ranging from Magnetic to Optical

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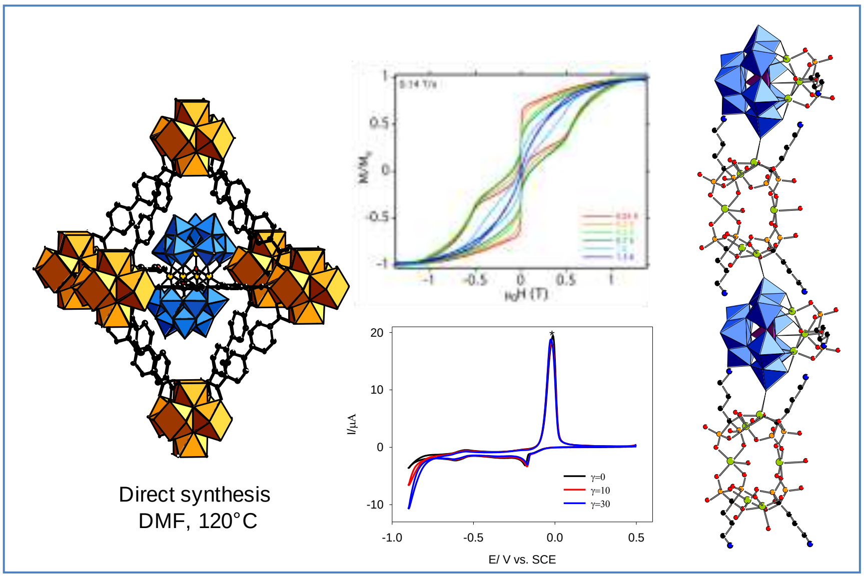
Abstract

The structural and chemical robustness as well as the tunability of POM materials allow to prepare highly stable composites such as fluorescent molecular switches,[1] POM@Metal Organic Frameworks Single Molecule Magnets[2] or efficient nitrates or O_2 reduction electrocatalysts.[3]



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Mixed-valence Polyoxometalate; a molecular nanoparticle for macroscopic electrical properties

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Abstract

Polyoxometalates (POMs) are one class of materials that belong to molecular nanoparticle. Their shape, size and composition are unique and uniform compared to traditional colloidal nanoparticles.[1-2] Also, high crystallinity and solubility that are originated from ionic character enable facile fabrication of multi-dimensional regular array. These structural uniqueness can offer development of nanomaterials science, due to high certainty and stability of property, reduction in scale from nano to molecular size and low cost fabrication protocols. However, it has been known that POMs have a low ability in inter-cluster interaction that involves electrostatic interaction, hydrogen bond and vdW interaction. Thus, uniqueness of POMs is generally not appeared in macroscopic properties such as charge transport, structural transition, long range ordering of electron, spin and dipole. By unveiling these isolated systems, we have been developed macroscopic electrical properties for molecular nanoparticle arrays by tuning nature of POM and counter cation.[3] Among them, long range electronic conduction through POMs and dielectric relaxation triggered by short range fluctuation of electrons trapped in POMs will be discussed.

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Metal-substituted polyoxometallates as artificial nucleases

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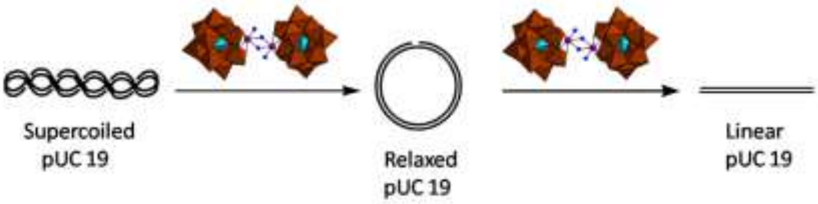
Abstract

The development of artificial nucleases represents an area of significant interest. However due to the extreme stability of phosphodiester bond in DNA, with a half-life for hydrolysis that has been estimated to be 130,000 years under physiological conditions, development of chemical agents for controlled DNA hydrolysis is a challenging task[1]. A number of metal complexes were reported to be able to hydrolyze phophodiester bonds of DNA, an despite the variety in the nature of metal ions and the ligands in the design of artificial metallonucleases, all metal complexes reported so far carry positive charge, which is assumed to be essential in driving the binding to the highly negatively charged DNA backbone.

We have recently shown that Ce(IV) and Zr(IV) substituted polyoxometallates (POM) promote effective hydrolysis of phosphoester bonds in RNA and DNA model systems[1-3]. Moreover we demonstrate that $[\{\alpha\text{-}PW_{11}O_{39}Zr(\mu\text{-}OH)(H_2O)\}_2]^{8-}$ (ZrK 2:2) is able to hydrolytically cleave plasmid pUC19 (pUC19) DNA under physiological pH. The interaction between ZrK 2:2 and DNA was proven by Circular Dichroism (CD)and ^{31}P NMR Diffusion Ordered Spectroscopy (DOSY).



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3.H. G. T. Ly, P. Shestakova, G. Absillis, T. N. Parac-Vogt* *Inorg Chem* DOI: 10.1021/acs.inorgchem.6b00385

Induced Chirality and Chirality Transfer in Polyoxometalate Systems

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Abstract

Inherent chiral polyoxometalates (ICPOMs), as nano-sized inorganic clusters with asymmetric frameworks, possess special features and display potential applications in heterogeneous enantioselective catalysis, sensing, optics and nanotechnologies. In comparison to those ICPOMs, a large majority of general POMs do not have asymmetric structures that show chirality. Therefore, there are important issues referring to the chirality of POMs such as how to donate chirality to achiral POMs and how to keep avoid the racemization of POM enantiomers in aqueous solutions so as to realize the functional properties of chiral POMs, and so forth.

Under the assistance of chiral supports through electrostatic interaction, we realized the induced chirality of achiral POMs both in organic phase and in aqueous phase, the stabilization of chiral frameworks, the chirality transfer from chiral POMs to metal nanoparticles, chiral heteropoly blue, and the asymmetric catalysis. Following the similar strategy, we made further development recently. Firstly, through host-guest interaction, the chirality transfers was realized from cyclodextrin to protonated 1-adamantanamine and finally to achiral POMs via electrostatic interaction.[1] The electrochemical modulation was used for the controlling single- and multi-electron redox of the POMs. Secondly, through the co-adsorption on metal nanoparticles and charged surface, we realized the chirality transfer between chiral POM and achiral POMs. Thirdly, by increasing the concentration of chiral POMs, we can also perform the chirality transfer from POM to POM in aqueous solution.[2] These research results demonstrate a possibility to use POMs as the chiral ligand for broadening functional applications of ICPOMs in diverse solution and solid systems.

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Mechanism of Self Assembly of Gigantic Inorganic Clusters

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Abstract

How do gigantic inorganic clusters form? If one considers, at the most simplistic level, the unique combinatorial arrangements of just the metal atoms in the largest known POM cluster, a cluster containing 368 Mo atoms, the number of arrangements (assuming 6 possible arrangements per metal centre) is of the order of $6^{368} = 2.289 \times 10^{286}$. This is a simply ludicrous number (and the absolute upper limit since there will be a vast number of geometrically degenerate identities as the linkages are not independent). Yet, if one considers the number of unique combinatorial arrangements of the simple Keggin ion, a cluster containing 12 Mo atoms, the number of arrangements is a more tractable $6^{12} = 2.18 \times 10^{9}$, see Figure.

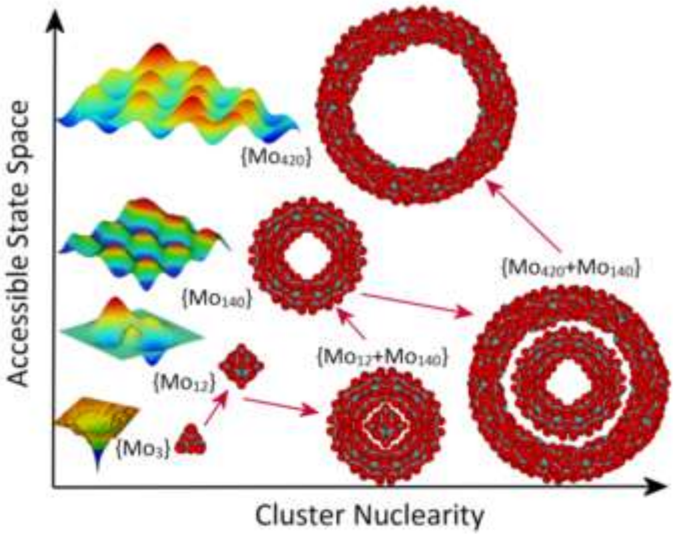

Figure Plot of accessible state space against cluster nuclearity. POM clusters have teal Mo atoms and red O ligands. As the cluster nucleairty increases, the state space which contains the number of combinatorial possibilities increases to an effectively infinite number which means the unaided assembly of high nuclearity clusters is effectively impossible.

In this talk I will explain the mechanism by which ‘impossible’ clusters can form.

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Polyoxometalate-functionalized nanocarbon as energy materials

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Abstract

Composite materials on the basis of polyoxometalates (POMs) and nanostructured carbon such as carbon nanotubes (CNTs) or graphene have attracted widespread attention as they combine the unique chemical reactivity of POMs with the unparalleled electronic properties of nanocarbons. The exceptional properties of these composites have been employed in catalysis, energy conversion and storage, molecular sensors and electronics. Herein, we report the research progress of our group in POM/CNT and POM/graphene nanocomposites with a focus on energy materials for batteries and supercapacitors.

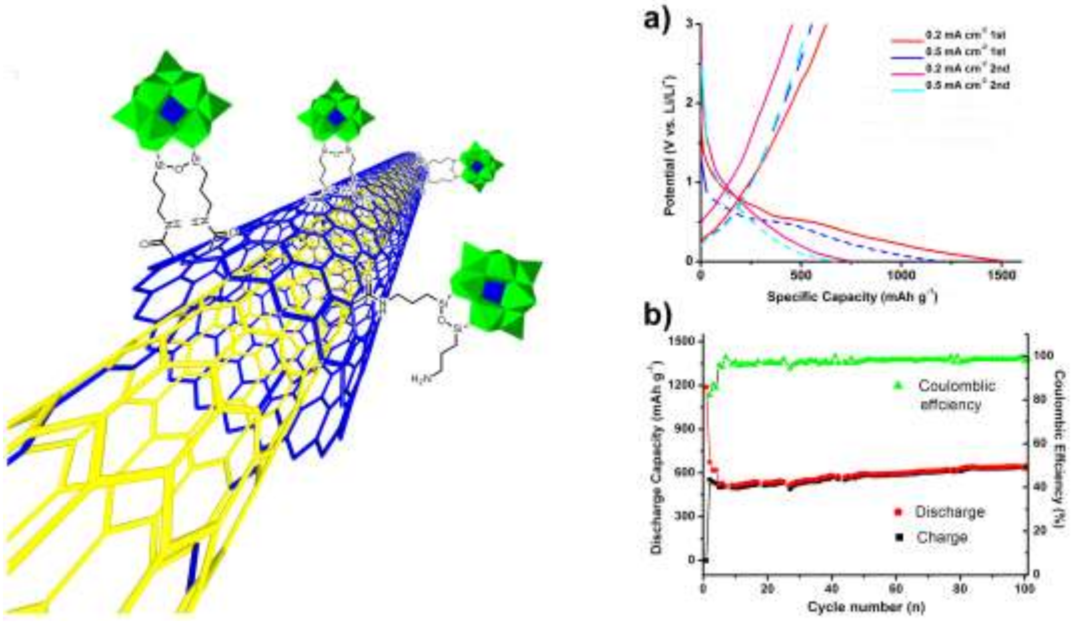

Figure. The application of covalently modified carbon nanotubes as anode materials; The 1st and 2nd charging and discharging curves of the lithium rechargeable battery; the discharge capacity and Coulombic efficiency vs cycle number; current density is 0.5 mA cm^{-2}

Magnetic polyoxometalates for quantum technologies

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Abstract

Magnetic polyoxometalates have shown to provide ideal model systems in molecular magnetism. In a first step these metal-oxide clusters were useful to study the magnetic exchange interactions and electron transfer processes at the molecular level. More recently, they have provided unique examples of single-molecule magnets. In particular, the lanthanoid based polyoxometalates have shown to be an excellent platform to rationalize and even to predict the properties of single-ion magnets from models that take into account the coordination geometry around the lanthanide ion [1]. These previous results have now opened the way to use these quantum objects in quantum computing. In this talk we will summarize the initial steps in this direction. This includes the use of POMs as molecular spin qubits exhibiting large coherence times [2] and the design of quantum processors based on these single-ion magnets.

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K24

Donor-Acceptor Organo-Imido POMs: New Materials for Photonics and Solar Energy Conversion

Ahmed Al-Yasari,[1,4] Hani El Moll,[1] Nick Van Steerteghem,[2] Chris Wood,[3] Fiona Black,[3] Bruce S. Brunschwig,[4] Elizabeth A. Gibson,[3] Koen Clays,[2] and John Fielden.*[1]

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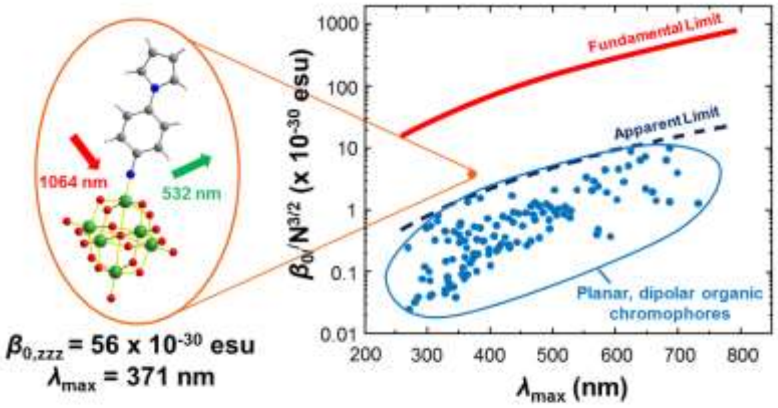
Compared to other POM-organic linkages, the POM-organoimido bond offers unusually strong electronic coupling between organic and inorganic fragments. Moreover, while the synthetic methods to obtain this class of POM derivatives are now quite well developed,[1] there have so far been few efforts to *experimentally*[2] address the properties that may emerge from this strong POM-organic communication.



Our Hyper-Rayleigh scattering (HRS) measurements[3] indicate that organoimido-POMs break through empirical non-linear optical performance limits[4] (see Figure) that apply to the vast majority of purely organic materials. These are supported by other spectroscopic techniques elucidating the role of the POM. Other, preliminary results show that related compounds have potential for use as electro-active co-absorbents in NiO-based p-type dye-sensitized solar cells.

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Optical and electrical properties of molecular junctions and networks.

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Abstract

First, I will discuss new molecular switches designed, synthesized, and used to form self-assembled monolayers (SAM) on gold as well as Nano-Particle Self-Assembled Networks (NPSANs) with high ON/OFF conductance ratios [1,2]. I will also present how we used these NSPANs to demonstrate an optically-driven reconfigurable boolean molecular circuit and a high-order harmonic generator for reservoir computing [3]. Then, I will present the properties of molecular junctions fabricated on a large array of sub-10 nm single crystal Au nanodot electrodes, each junction being made of less than one hundred molecules [4,5]. Thanks to this approach, I will discuss some pending issues in molecular electronic : effects of mechanical strain [6] and of inter-molecular interactions on the conductance of molecular junctions [7], demonstration of molecular electronic devices for high-frequency operation with a molecular diode working in the microwave regime up to 17 GHz [8]. Finally, recent charge transport measurements on POMs-based molecular junction on Au and silicon will be presented.

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Why Do Highly-Charged Polyions with Univalent Counterions Form Spherical Shells – an Unanswered Question?

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Abstract

Tianbo Liu and coworkers have demonstrated that a wide variety of highly-charged polyions with univalent counterions can form spherical shells in aqueous solution, including poloxometalates, coordination cages, and polysilicates. The question of why these spherical shells are formed has been addressed by Willem Kegel and coworkers assuming short-range attraction and long-range repulsion between polyanions. An alternative is presented where short-range repulsion and long-range attraction are assumed.

Organic-Inorganic Surfactants: Hybrids with Polyoxometalate Heads and Beyond.

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Abstract

Surfactants are molecules of enormous scientific and technological importance, which are widely used as detergents, emulsifiers or for the preparation of diverse nanostructures. Fascinating abilities regarding the formation of self-organized structures, like micelles or liquid crystals, originate from their amphiphilic architecture, which comprises a polar head group linked to a hydrophobic chain. While almost all known surfactants are organic, a new family of surfactants is now emerging, which combine amphiphilic properties with the advanced functionality of transition metal building blocks.[1] The current presentation will cover inorganic surfactants (I-SURFs) containing multinuclear, charged metal-oxo entities as heads (Fig. 1),[2] and their exploration with regards to additional functionalities. A particular challenge is the creation of smart surfactant systems that can be controlled via external stimuli.[3] The unique properties of I-SURFs for unusual self-assembly will be addressed.[1-3] The presentation will close with our most recent work on conducting, magnetic and catalytic I-SURFs.[4]

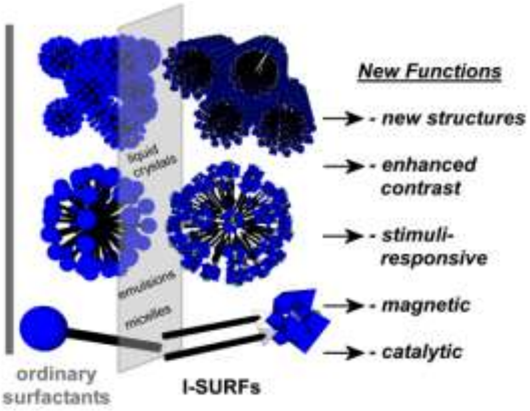

Figure 1. Surfactants with inorganic heads (I-SURFs) which unlike ordinary surfactants possess a set of additional, unique properties.

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Directed Self-Assembly, Electronic Modulation and Isomer "locking" in POM systems.

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Abstract

Polyoxometalates (POMs) have attracted the attention of many research groups during the last 25 years due their remarkable structural motifs, electronic properties[1] and also the potential application in scientific fields. In this talk, I discuss the assembly of Dawson-like mixed metal (Mo/V) fanily of molecular capsules of the general formula, $[Mo^{VI}_{11}V^{V}_{5}V^{IV}_{2}O_{52}(XO_3)]^{7-}$ where X = HP; Te; Se; S and their modulation of their electronic properties induced by the pyramidal templates.[2] Moreover, I discuss the synthesis and characterization of the first members of the δ-Keggin polyanionic isomers, with the general formula: $TEAH_pNa_q$ $[H_2M_{12}(XO_4)O_{33}(TEA)]\cdot rH_2O$[3] and the cation-modulated photochemical process upon illumination, observed as SC-to-SC transformation studied by X-ray diffraction.

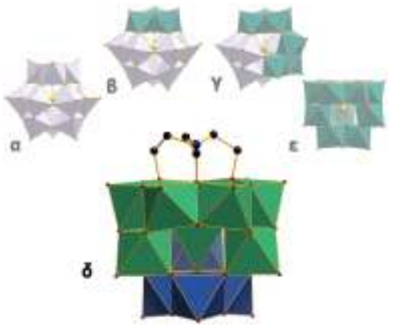

Figure 1. Ligand induced entrapment of the *δ*-Keggin structure.

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Revisiting some polyoxometalate archetypes

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Abstract

Polyoxometalate archetypes such as the $\{P_8W_{48}\}$ ring cluster are commonly associated with high formation tendency and stability, and limited electron density on peripheral oxygen positions, subsequent functionalization by e.g. incorporation of heterometals typically is restricted to specific coordination sites. Recent interest in certain magnetic $\{P_8W_{48}\}$ derivatives motivated us to revisit the $\{P_8W_{48}\}$ reaction system, revealing surprising reactivity, novel structure types, and the need for some corrections to the existing literature. Finally, we will also highlight strategies to, literally, squeeze new magnetic properties out of well-established magnetic POMs.

Water Oxidation Catalysis with Oxoclusters: From POMs to Cubanes

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Abstract

Water oxidation remains the challenging part of artificial photosynthesis as a promising approach to store solar energy resources directly in chemical fuels. Development of economic water oxidation catalysts (WOCs) based on earth-abundant metals is a forefront endeavor, and polyoxometalates (POMs) have attracted intense interest as tunable all-inorganic WOCs.[1] We investigate their challenging structure-activity relationships, and our studies of sandwich-type cobalt-containing tungstobismutates showed that subtle disorder in the transition metal core can be decisive for the WOC activity.[2] Next, we selectively prepared Co-containing POMs in search of correlations between WOC activity and steric accessibility of Co centers. Screening of Cu-POMs as WOC prototypes brought forward a series of new structural motifs with increasing dimensionality (Fig. 1).[3] Parallel investigations into Keggin-type $[Ni(H_2O)XW_{11}O_{39}]^{n-}$ (X = P, Si, Ge) POMs as visible-light-driven water reduction catalysts further underscored the complex role of POMs in photocatalytic water splitting due to their interaction with $[Ru(bpy)_3]^{2+}$ as the most widely used photosensitizer.[4]

Fig. 1. Transition metal-based POM architectures: toward water oxidation catalysts.

This inspired us to develop neutral cobalt cubane clusters as bio-inspired WOCs, namely $[Co^{II}_4(hmp)_4(\mu\text{-}OAc)_2(\mu_2\text{-}OAc)_2(H_2O)_2]$ (hmp = 2-(hydroxymethyl)pyridine)[5a] and the $[Co^{II}_3Ln(hmp)_4(OAc)_5H_2O]$ ($\{Co^{II}_3Ln(OR)_4\}$ (Ln = Ho – Yb) family.[5b] Their catalytic performance and mechanisms are compared to representative Co-POMs.

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Polyoxometalate composites for heterogeneous water oxidation catalysis

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Abstract

The realization of artificial photosynthesis for the production of renewable environmentally friendly fuels will need to overcome several hurdles to compete and eventually substitute fossil fuels in the long term. One of the main problems remains the lack of fast, robust and readily available catalysts to promote hydrogen and oxygen evolution at technologically relevant rates and environments. Oxygen evolution from water oxidation is a particularly demanding reaction since it occurs at very high oxidation potentials involving four electrons to make a relatively weak oxygen-oxygen bond. Furthermore, efficient water oxidation catalysts (WOCs), able to work at low overpotential for optimized energy conversion, will also need to be stable to air, light, water, heat and oxidative deactivation.

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \quad E = +1.229 - 0.059\,(\mathrm{pH})\,\mathrm{V} \text{ vs NHE at } 25^\circ\mathrm{C} \quad (1)$$

The state-of-the-art in WOC research is lead by robust (although slow) heterogeneous metal oxides; and by fast homogeneous coordination complexes, where the presence of organic ligands precludes long-term stability under turnover conditions because of oxidative deactivation. Combination of fast reaction kinetics with robust performance is still far from being achieved, and only noble metals are offering technologically relevant results.

Polyoxometalates (POMs) appear as a promising solution where the fast kinetics of molecular catalysts may be combined with the robustness of inorganic solids, due to their purely inorganic nature. Indeed, several POM-based WOCs have been reported in recent years with excellent performances.[1,2,3]

Here we will present our latest results on the WOC activity of POMs based on earth abundant metals, showcasing their processing onto solid supports for the development of modified heterogeneous electrodes. Processing and solid state performance will become crucial for their implementation into artificial photosynthetic platforms, where only heterogeneous systems may reach technological impact.

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Polyoxometalates as functional building blocks

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Abstract

Systematic routes to the functionalization and post-functionalization of polyoxometalates (POMs) have been developed,[1] so that we are now handling a library of organic-inorganic POM-based hybrids that allow us to investigate otherwise their potential in molecular materials. Examples dealing with the use of POMs as support for single site catalysis,[2] with covalent anchorage of POMs onto mesoporous solids for catalysis [3] or related to the field of molecular electronics with the elaboration of densely-packed monolayers of electroactive POMs onto electrodes, including silicon [4] and graphene [5] will be presented in a first part.

In a second part, we will discuss the insertion of POMs as structuring agents in magnetic nanocrystal lattices. We will describe the co-assembly of oleic-acid capped γ–Fe_2O_3 nanocrystals (NCs) and Keplerate-type POMs $[Mo_{132}O_{372}(CH_3COO)_{30}(H_2O)_{72}]^{42-}$ $\{Mo_{132}\}$ associated to long-chain alkyl-ammonium cations. POMs have proved to enhance the long range ordering of the NCs and as tunable spacers to tune the dipole-dipole interactions between the NCs.[6] The use of functionalized POMs offers new perspectives to trigger the POM-NC interactions, while combining the physical properties of the POMs and NCs opens the way to the design of multifunctional materials

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Polyoxometalate complexes of metal-oxide nanocrystals

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Abstract

Building on recent investigations of electrostatically stabilized POM ligand shells on metal(0) nanoparticles, we report a conceptually new role for POM cluster-anions as covalently coordinated redox-active ligands in polyanionic “complexes” of metal-oxide nanocrystals, giving isolable, water-soluble nanostructures uniquely positioned between molecular macroanions and traditional—electrostatically stabilized — colloidal metal oxides. In POM complexes of TiO_2, for example, numerous Ti(IV)-substituted POM capping ligands, “$[\alpha\text{-}XW_{11}O_{39}Ti]–O^{–}$” (X = $Al^{3+} < Si^{4+} < P^{5+}$) are covalently attached to ca. 6-nm anatase-TiO_2 cores. Using cryogenic transmission electron microscopy (cryo-TEM), in combination with the large electron densities of the capping-ligand W (Z =74) atoms, we provide the first direct images of protecting ligands on colloidal metal-oxide nanocrystals. Functionally, the covalently attached POMs serve as tunable electron-accepting ligands, and in a model photochemically driven hydrogen-evolution reaction, the soluble hybrid materials are an order of magnitude more reactive that either TiO_2 or POMs alone, with reactivities increasing in the order, X = $Al^{3+} < Si^{4+} < P^{5+}$. The mechanistic basis for this ordering, and for the enhanced reactivity itself, will be discussed, followed by new findings documenting the preparation and diverse reactions of analogous hybrid materials with nano-scale cores of other transition- and main-group metal oxides or oxy-hydroxides. The latter findings show that POM complexes of TiO_2 represent but one (first documented) member from an emerging family of related hybrid materials, each with unique chemical, electrochemical or photochemical properties and reactivities. Hence, just as traditional ligands control catalytically active *metal centers* in *molecular* complexes, the tunable redox chemistries and photochemical properties of covalently attached POM capping ligands now provide new options for rationally controlling metal-oxide mediated electron-transfer processes.

Molecular Metal Chalcogenides for Energy Conversion and Storage

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Energy conversion and energy storage are critical research themes of the early 21st century. Inorganic chemistry can provide sustainable answers to many pressing questions such as solar energy conversion or electrochemical energy storage by giving access to new, technologically relevant materials whose properties can be designed on the molecular level. Prime examples are molecular metal chalcogenide clusters, where redox-active, earth abundant metals (e.g. V, Mo, W, etc.) are linked into a finite framework by chalcogenide (e.g. oxido or sulfido) anions.[1] This presentation will show how this vast compound class can be employed in energy conversion and energy storage materials, focusing on light-driven water splitting A bio-inspired manganese vanadium oxide cluster, $[Mn_4V_4O_{17}(OAc)_3]^{3-}$ is presented which is capable of catalyzing the visible light-driven water oxidation together with a $[Ru(bpy)_3]^{2+}$ as photosensitizer. The system is a functional model for the natural oxygen evolving complex and could provide valuable insight into the redox chemistry used in nature to oxidize water.[2] As second example, a molybdenum sulfide anion $[Mo_3S_{13}]^{2-}$ is presented as highly active hydrogen evolution catalyst under light driven conditions, together with initial mechanistic insight into catalyst deactivation and possible catalyst repair under operating conditions. Using this approach, turnover numbers up to 24,000 and turnover frequencies up to 2.5 s^{-1} are observed.

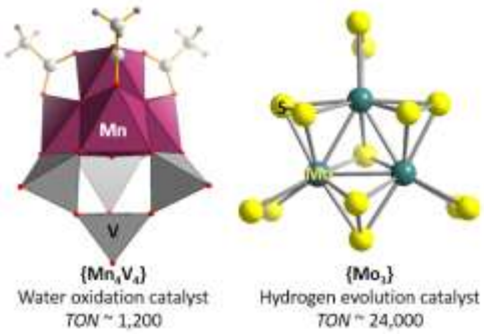

Fig. 1 : Examples of molecular metal chalcogenides used in energy conversion and energy storage systems.

In summary, this presentation will explore the emerging possibilities of molecular metal chalcogenides as viable models and alternative technological materials for diverse applications in energy conversion and storage. General principles leading to their reactivity will be explored and current limitations needing urgent research will be highlighted.

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Porphyrin-Polyoxometalate Electropolymers for the Photoelectrochemical Energy Conversion

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Abstract

The development of hybrid polymers incorporating POMs is a promising approach to elaborate new functional materials. POMs can undergo multi-electron redox processes without decomposition, which are the basis for numerous catalytic processes. Unfortunately, in most cases POMs reach excited states only under UV irradiation. To expand the practical applications, their association to a visible-light photosensitizer via non-covalent, or covalent bonding is so far a prerequisite since POMs themselves are mainly photoactive in the UV domain of the solar spectrum, which strongly limits the use of POMs in solar visible light conversion materials. In this context, we have developed a method of electropolymerization based on nucleophilic attacks of bipyridinium-substituted porphyrins onto electrogenerated porphyrin dications [1] which can lead to the formation of hybrid POM-porphyrin copolymeric films (Fig. 1) obtained by the electro-oxidation of porphyrin in the presence of the POM bearing two pyridyl groups (Py-POM-Py) [2]. This process is feasible for other POMs functionalized with two pendant pyridine groups such as Dawson, Lindqvist or Keggin type POMs [3-4].

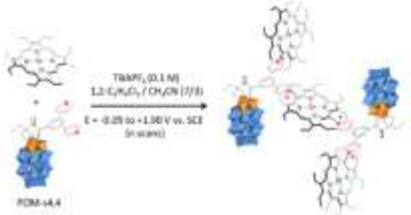

Fig 1. Example of copolymer.

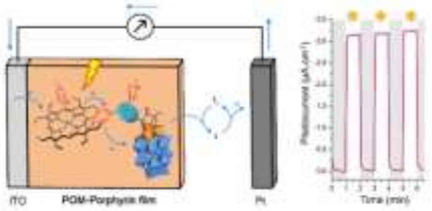

Fig 2. Photoelectrochemical response in aqueous solution.

A second methodology is also proposed to form hybrid POM-porphyrin films: first the formation of cationic poly-porphyrin electropolymer, and then by metathesis reaction, the (partial) exchange onto the surface of the initial counter ions (PF_6^-) by the POM^{n-}. The electropolymers are studied by spectroelectrochemistry (UV-vis-NIR-IR), EQCM, AFM, XPS and impedance measurements (EIS). Their photovoltaic performances have been also investigated under visible-light illumination [5-7].

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Decavanadate Based Hetero-metallic Inorganic-organic Hybrids as Highly Active Electrocatalysts for Hydrogen Evolution

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Abstract

Polyoxometalates (POMs), a class of redox facile metal-oxy anion clusters, are steadily emerging as efficient, cheap, precious-metal-free electrocatalysts for hydrogen evolution reaction (HER).[4,5,6] We have synthesized, three decavandate ($V_{10}O_{28}^{6-}$) based supramolecular inorganic-organic hybrids (**1**, **2** and **3**) using different ligands (2,2'-bipyridine: **1**, 4-amino pyridine: **2**, and ethylene diamine: **3**) and Cu as the secondary transition metal (only in **1** and **2**) for electrocatalytic HER applications. Single crystal analysis revealed that in **1**, the Cu atom (octahedrally coordinated) was directly linked to the decavanadate unit while in **2**, Cu formed a separate octahedral complex that was linked to the decavanadate unit only through non-covalent interactions. Hybrid **3** exhibited excellent HER activity as cathode in acidic media with an onset overpotential of only 120 mV, charge transfer resistance (R_{CT}) as low as 580 Ω at -160 mV (vs RHE) and the catalytic current density of 10 $mA.cm^{-2}$ was reached at an overpotential of 260 mV. The Tafel slope, 121 $mV.dec^{-1}$, indicates that Volmer step is the r.d.s for HER in case of **3**. The comparative activity order followed as 3>2>1, where the onset overpotential for **2** and **1** were at 180 mV and 280 mV respectively. The trend suggests that there is a synergistic effect of both the transition metals (Cu and V) towards the catalysts' HER activity. Theoretical and experimental studies are going on to understand the role of structural, electronic and conductive properties of the three hybrids in determining their relative HER activity.

* corresponding author

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New Perspectives for Old Clusters: Anderson–Evans Anions as Building Blocks of Heterometallic 3d–4f POM Frameworks

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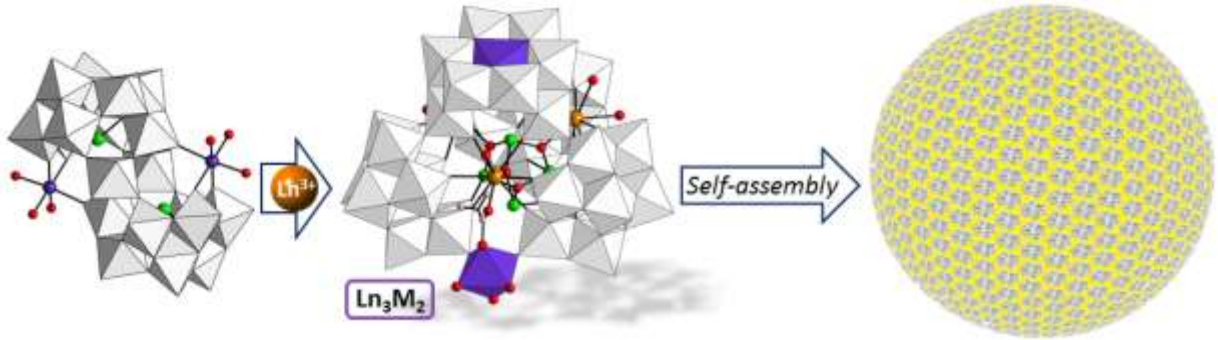
Abstract

One of the most rational synthetic strategies to prepare heterometallic 3d–4f polyoxometalates (POMs) consists in the combination of lanthanides with 3d-metal-substituted POM precursors. Following this route, a series of nine $[Sb_7W_{36}O_{133}Ln_3M_2(OAc)(H_2O)_8]^{17-}$ anions (**Ln_3M_2**; Ln = La–Gd, M = Co; Ln = Ce, M = Ni and Zn) have been obtained by reacting 3d metal disubstituted Krebs-type tungstoantimonates(III) with early lanthanides [1]. Their unique tetrameric structure contains a novel $\{MW_9O_{33}\}$ capping unit formed by a planar $\{MW_6O_{24}\}$ fragment to which three $\{WO_2\}$ groups are condensed to form a tungstate skeleton identical to that of a hypothetical trilacunary derivative of the ε-Keggin cluster. It has been shown for the first time that classical Anderson–Evans $\{MW_6O_{24}\}$ anions can act as building blocks to construct purely inorganic large frameworks. Unprecedented reactivity in the outer ring of these disk-shaped species is also revealed. The solution stability of the clusters have been confirmed by ESI-MS and their ability to self-associate in *blackberry*-type vesicles in solution has been assessed for the **Ce_3Co_2** derivative.



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Lacunary Heteropolytungstates Stabilizing Polynuclear Magnetic 3d-Transition Metal Cores

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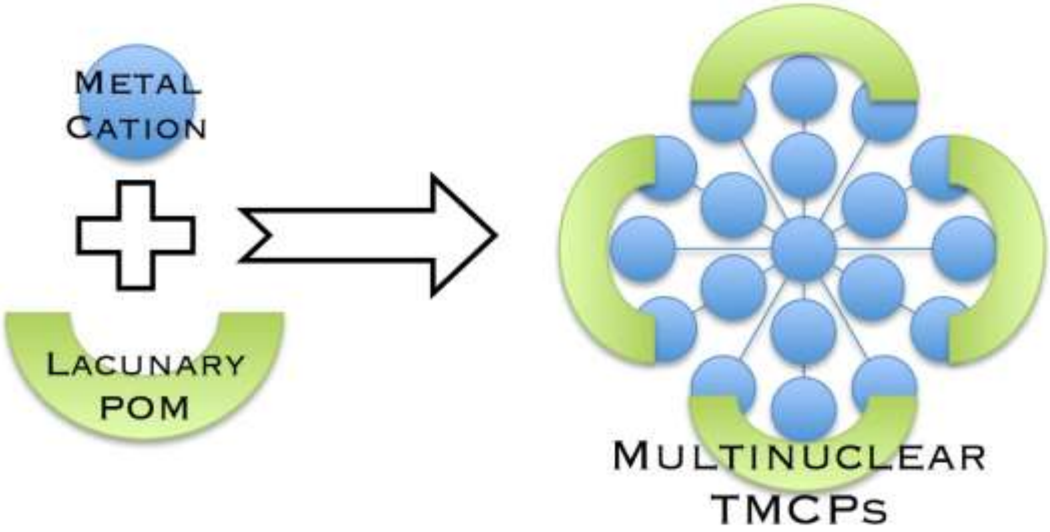
Tricalunary heteropolytungstate precursors are inorganic ligands that can coordinate to electrophilic centers such as 3^d-transition metal ions.[1] Paramagnetic transition metal-containing polyoxometalates (TMCPs) are of special interest for their magnetic and catalytic properties, and the challenge remains in synthesizing novel, multi-centered 3*d*-paramagnetic assemblies stabilized by lacunary heteropolytungstates.[2] Here we report on some novel multinuclear TMCPs synthesized by our group.[3]



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Importance of Specific Metal-Polyoxometallate Interactions in Efficient Charge Propagation and Electro(photo)catalysis

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Of particular interest to the preparation of advanced catalytic materials is efficient utilization of carbon nanostructures and noble metal nanoparticles, their stabilization and intentional activation, as well as organization into two-dimensional arrays, ultra-thin films or three-dimensional networks (e.g. through sequential attraction) on electrode surfaces. They can form nanosized materials with well-defined composition, structure and thickness that exhibit electrocatalytic properties toward oxidation of methanol, ethanol or dimethyl ether. We explore here the ability of inorganic structures to stabilize and derivatize metal and carbon nanostructures. Here certain nanostructured inorganic oxides (e.g. WO_3, MoO_3, TiO_2, ZrO_2, V_2O_5, and CeO_2) and polyoxometallates of molybdenum or tungsten influence supported metal centers in ways other than simple dispersion over electrode area. Evidence is presented that the support can modify activity (presumably electronic nature) of catalytic metal nanoparticles thus affecting their chemisorptive and catalytic properties. Metal oxide nanospecies can generate –OH groups at low potentials that induce oxidation of passivating CO adsorbates (e.g. on Pt); they can potentially break C-H or C-O bonds (e.g. by hydrogen tungsten oxide bronzes); and they can possibly weaken C-C bonds during ethanol oxidation (e.g. through changes of the electronic properties of Pt).

Our research interests also concern development of systems for reduction of carbon dioxide. For example, instead of conventional Pd nanoparticles, nanosized Pd immobilized within ultra-thin films of polyoxometallates and their salts have been considered. Reduction of carbon dioxide begins now at less negative potentials and is accompanied by significant enhancement of the CO_2-reduction current densities. Among important issues are specific interactions between hydroxyl and metal-oxo centers and metallic palladium sites at the electrocatalytic interface.

When it comes to photoelectrochemical water splitting, we demonstrate here utility of gold nanoparticles (modified or stabilized with Keggin-type and ruthenium-containing polyoxometallates, $PMo_{12}O_{40}^{3-}$, as capping agents) to enhance photocurrents generated by mesoporous tungsten trioxide, WO_3, photoanodes irradiated with visible light in aqueous solutions. To demonstrate generation of localized surface plasmons, we have performed measurements using scanning near-field optical microscope (SNOM). The mechanism for the interaction between the gold plasmons and the semiconductor is complex but sound.

We will also show that nano-electrocatalytic polyoxometallate-based systems are of importance to the development of the effectively operating iodine-based charge relays in dye sensitized solar cells and in molecular electronic (charge storage) devices.

Colloids of POMs as a Mechanistic Step for Chemical Reactivity

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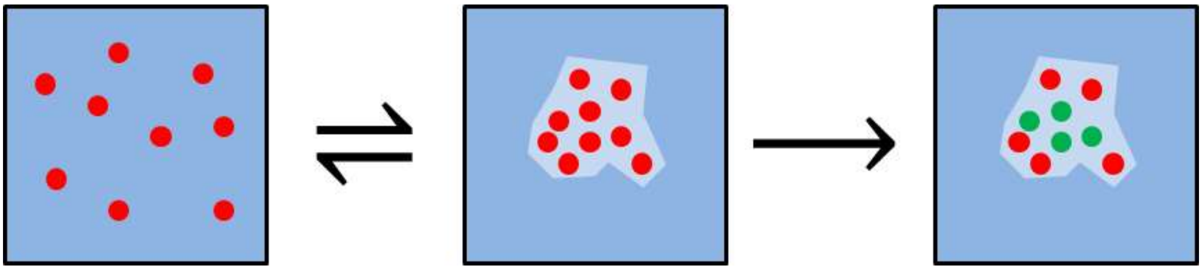
Abstract

It has been known for some time that large Keplerate type POMs form blackberry type colloids in solution[1]. Recently we showed that also smaller quasi Wells-Dawson type polyfluoroxometlates (PFOMs) form colloids under high concentrations or upon addition of precipitating counter-ions to solution[2]. Moreover, it has been shown that an oxygen formation chemical reaction that requires four such PFOMs for completion was catalyzed by the formation of these colloids. The formation of colloids in this case was controlled by addition of alkali chlorides, where the more precipitating Cs^+ caused the formation of larger colloids and the less precipitating Li^+ did not form any colloids in solution.

This result encouraged us to think of other chemical reactions where collisions between a few POM molecules are required and see if they too have a mechanistic step of colloid formation. Specifically, the self-assembly of POMs is such a reaction where oxides of single W or Mo atoms coagulate to form polyoxometalate complexes containing a large number of these atoms. These self-assembly reactions are performed at high concentrations and usually show signs of aggregation that is later redissolved. We propose that POM self-assembly goes through a dense liquid phase mechanism where small pieces aggregate randomly in the first step and a subsequent ordering occurs on the second step.



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Complex Assembly of $\{Cu_6\}$-Incorporated Icosametallic Clusters

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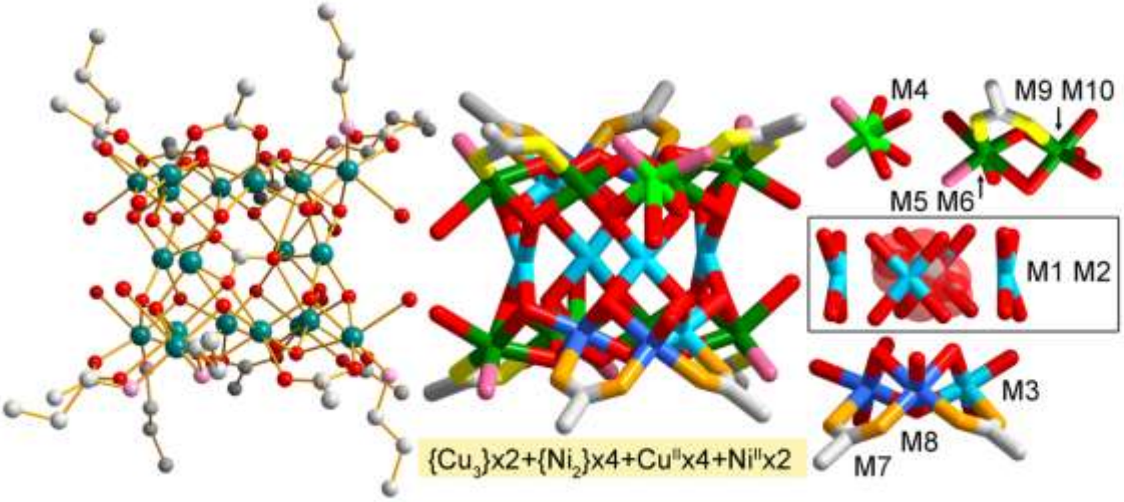
Abstract

Self-assembly of the nanospheric icosanuclear copper-based oxo-clusters ($\{M_{20}\}$) has drawn much attention recently. Besides the first example of $\{Cu_{12}La_8\}$[1] and a polyanion $\{Cu_{20}\subset W_{48}\}$,[2] another three discrete clusters with the $\{Cu_{20}\}$ core were isolated by different synthetic paths and peripheral ligands, indicating the favoring formation of $\{Cu_{20}\}$ in solution.[3-5] While it has been demonstrated that the heterometallic $\{Cu_{20}\}$-derived clusters with a fixed copper-to-metal ratio, 12:8, are achievable by mixing Cu(II) with Zn(II), La(III) or Mg(II), our studies revealed the assembly of Cu-Ni and Cu-Co icosanuclear clusters with a "question-raising" metal ratio of 1:1, indicating that the assembly mechanism of $\{Cu_{20}\}$-derived clusters is more complex than expected.[6] On the basis of metal bricks' coordination modes, thermodynamic stability of M-N dative covalent bonds and the kinetic accessibility of components, a plausible Cu-Ni structure composed of a few distinct components was proposed. It is noticeable that the $\{Cu_6\}$ moiety templated by CO_3^{2-} is shared in all found $\{Cu_{20}\}$-derived structures, possibly serving as a scaffold for the self-assembly. These structural analyses suggest that $\{Cu_{20}\}$-derived clusters may be an important object of research in self-assembly of molecular clusters with addressable complexity.



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The Wells-Dawson Polyoxotungstates: re-exploring their electrochemical behaviour in solution.

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Abstract

Thanks to the many possibilities of composition and structure, which result in unique redox properties, polyoxometalates (POM) are excellent model compounds for the study of the mechanisms governing electron transfer between an electrode and a molecule. They are often implicated in reversible electron transfer processes associated or not to proton transfer, rendering them outstanding candidates for catalysis and electro-catalysis. Keggin-type and Wells-Dawson-type POM are the most frequently used systems for this kind of studies.

The reduction of $[\alpha\text{-}As_2W_{18}O_{62}]^{6-}$, $[\beta\text{-}As_2W_{18}O_{62}]^{6-}$ and $[\alpha\text{-}H_4AsW_{18}O_{62}]^{7-}$ was investigated using cyclic voltammetry in buffered aqueous solution over the pH range 1.0-8.0. Each compound underwent several proton-coupled electron transfers (PCET) characterized by a specific E-pH diagram. Quantitative thermodynamic studies of reaction mechanisms have been published for metal-substituted POM.[1,2] However such a systematic approach for non-substituted POM is scarce.[3,4] PCET is well described by a square–scheme mechanism which takes into account the thermodynamic standard values of the system. This study sheds light on the influence of the molecular isomerism and the number of hetero-element atoms on the electrochemical properties of the POM.

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Introducing Thallium in Polyoxometalate Chemistry

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The aqueous solution chemistry of Tl^{3+} is dominated by a high tendency for hydrolysis, resulting in the formation of Tl^{3+}-hydroxo complexes. Contrary to the lighter metal ions of group 13, Tl^{3+} does not form polynuclear hydroxo-complexes,[1] and compounds with more than one Tl atom are known mainly in organo-thallium chemistry.[2] Tl-containing compounds are widely used in electrical, medical, and even glass manufacturing industries[3].

The area of Tl-containing POMs is barely investigated. Some thallium salts of di-, para- and metatungstates have been prepared by conventional methods.[4] In 1953, Magneli[5] first described the structure of hexagonal tungsten bronze A_xWO_3, and later and Shivahare[4] (1964) and Bierstedt[6] (1965) isolated $Tl_{0.3}WO_3$ and $Tl_2W_4O_{13}$, respectively. These compounds are extended tungsten oxides and hence not classified as POMs. To date no structurally characterized discrete Tl-containing polyanion has been reported.

We were inspired by the above work, and thus decided to attempt incorporating thallium in a POM cluster. Herein we report the synthesis and structure of a thallium(III)-containing tungstosilicate. We also used Tl NMR and ESI-MS to study the solution stability of this compound.

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Palladate/Tungstate Hybrids

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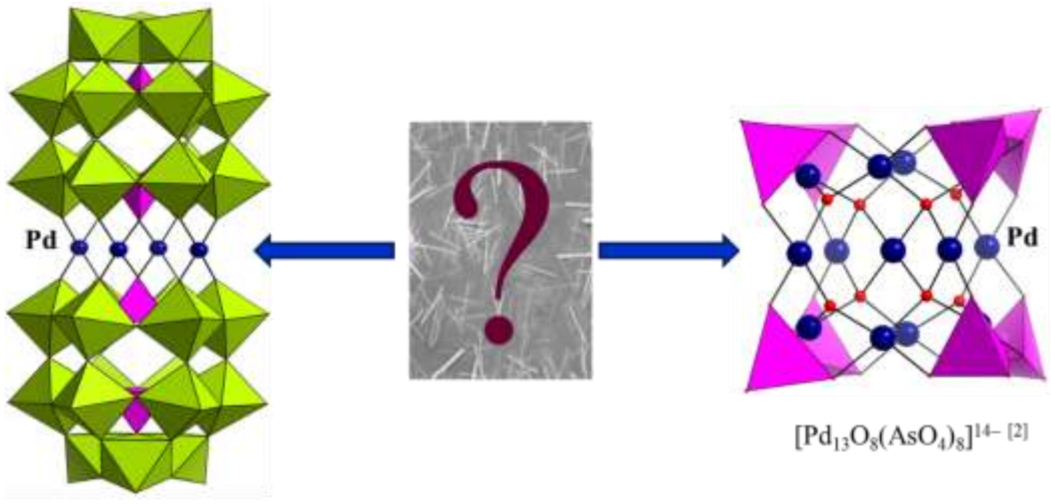
Abstract

Chemistry of palladium-containing polyoxometalates (POMs) has experienced an impressive development over the last ten years.[1] In particularly, a novel subclass of POMs built by square-planar Pd^{II} addenda ions has been discovered.[1-2] Here we report on a series of hybrid polyanions composed by both tungsten(VI) and palladium(II) addenda. These species possess various nuclearity and structures and make a logical link between "classical" area of Pd^{II} complexes of polyoxotungstates and novel subclass of POMs, polyoxopalladates. Solution behavior and reactivity of new compounds will be also discussed.



$[Pd_{13}O_8(AsO_4)_8]^{14-}$ [2]

$[Pd_4(P_2W_{15}O_{56})]^{16-}$ [3]

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Constructing high nuclearity polyoxotungstates with the aid of silver(I) counter-cation

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Abstract

Silver(I) ions are versatile in constructing, stabilizing and isolating new polyoxometalate architectures.[1-3] In this contribution, we present serval new high nuclearity polyoxotungstates that are formed with the aid of silver(I) counter-cations. One latest finding, for example, is the construction of $\{W_{63}\}$ and $\{W_{66}\}$ from the conventional 4-fold symmetric $\{P_8W_{48}\}$ of a drum-like ring structure consisting of four pieces of $\{P_2W_{12}\}$ subunits. Additional Keggin lacunary $\{PW_9\}$ or Dawson lacunary $\{P_2W_{12}\}$ building units are found to mount on the $\{P_8W_{48}\}$ drum top surface to form high nuclearity clusters $\{W_{63}\}$ or $\{W_{66}\}$. The $\{W_{63}\}$ and $\{W_{66}\}$ clusters co-crystallize with the two lacunary $\{PW_9\}$ and $\{P_2W_{12}\}$ parts with disorder located together in 1:1 ratio, revealed by structure determination. Resolving the disorder model is a big challenge with the identification of the heavy W and light O atom positions.

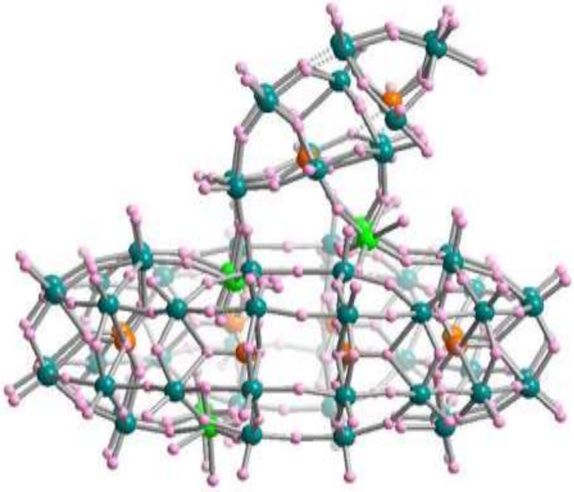

Figure 1 side view of the 4-fold symmetric $\{P_8W_{48}\}$ drum-like ring structure with 6 add-on positions (bright-green coloured) and both the Keggin lacunary $\{PW_9\}$ and Dawson lacunary $\{P_2W_{12}\}$ units disordered located on top sitting on the $\{P_8W_{48}\}$

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C12

Mono- and di-titanium-substituted Lindqvist tungstates as catalysts for heterolytic activation of H_2O_2

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Abstract

Ti-substituted polyoxometalates (POMs) are known for their remarkable catalytic activity in a range of selective oxidations with H_2O_2 as green oxidant [1]. Here we first report on the interaction of mono- and di-titanium substituted Lindqvist type tungstates, $(Bu_4N)_3[(MeO)TiW_5O_{18}]$ (TiW_5) and $(Bu_4N)_3[$*cis*-$(MeO)_3Ti_2W_4O_{16}]$ (Ti_2W_4), with hydrogen peroxide and their catalytic properties in alkene epoxidation with H_2O_2. TiW_5 [2] and Ti_2W_4 were synthesized by hydrolysis of a mixture of $Ti(OMe)_4$, $WO(OMe)_4$ and $(Bu_4N)_2WO_4$ in dry acetonitrile. The structures were confirmed by FTIR, ^{1}H and ^{17}O NMR. The interaction of TiW_5 and Ti_2W_4 with aqueous H_2O_2 in MeCN was monitored by UV-vis along with ^{17}O and ^{1}H NMR. The UV-vis study revealed that addition of water decelerated the formation of titanium peroxo complex from TiW_5 but produced no effect in case of Ti_2W_4. Titanium peroxo complexes were generated by adding an excess of H_2O_2 to TiW_5 and Ti_2W_4, isolated and characterized by FTIR, UV-vis, ^{17}O NMR and some other techniques.

Cyclohexene was used as a test substrate to probe catalytic performance of the Lindqvist Ti-POMs. Under turnover conditions, both Ti_2W_4 and TiW_5 gave mainly cyclohexene oxide, *trans*-1,2-cyclohexanediol and 2-hydroxycyclohexanone (59-70% total selectivity), indicating predomination of heterolytic mechanism of H_2O_2 activation over homolytic one. However, Ti_2W_4 was more active and selective than TiW_5. The addition of 1 equiv. of H^+ accelerated the oxidation reaction and improved both epoxidation selectivity (up to 83%) and H_2O_2 utilization efficiency (up to 69%). FTIR confirmed retention of the Lindqvist structure after the catalysis and revealed the formation of the $[(\mu\text{-}O)(TiW_5O_{18})_2]^{6-}$ dimer in case of TiW_5.

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Computational modeling of polyoxometalate-protein interactions

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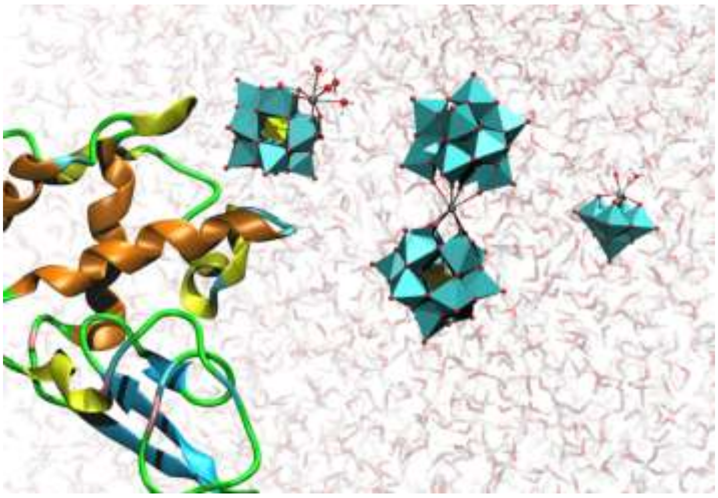
Abstract

Biological application is one of the emerging fields in polyoxometalate (POM) chemistry. POMs have shown anticancer and antibiotic activity; and also, they can be used as enzyme inhibitors, as “super-heavy atoms” in the crystal structure determination, and as selective peptidases. Although little is known about the exact molecular mechanism responsible for POM biological activity, the importance of their size, shape, charge and incorporated metal have been recognized.

Here we present the first atomistic analysis of the interactions between POMs and biomolecules, aiming to unravel the physicochemical foundations which govern these interactions. We performed molecular dynamics (MD) simulations on different POMs, selecting initially, the model protein hen egg lysozyme (HEWL). Our results agree with the X-ray characterization of non-covalent complex between HEWL and Zr-subtituted POM reported by Parac-Vogt *et al.*,[1] characterize the specific interactions, and establish a relationship between POM composition and protein affinity. We also present further computational studies on related aspects such as the mechanism of peptide bond hydrolysis and the behavior of POMs in the bulk.



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Detailed Mechanism of ATP Hydrolysis Promoted by a Binuclear Zr^{IV}-Substituted Keggin Polyoxometalate Elucidated by a Combination of ^{31}P, ^{31}P DOSY and ^{31}P EXSY NMR Spectroscopy

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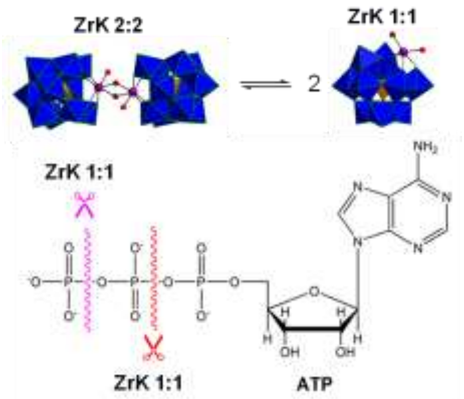
The full reaction mechanism of adenosine triphosphate (ATP) hydrolysis in the presence of the binuclear Zr^{IV}-substituted Keggin type polyoxometalate $(Et_2NH_2)_8[\{\alpha\text{-}PW_{11}O_{39}Zr(\mu\text{-}OH)(H_2O)\}_2]\cdot 7H_2O$ (ZrK 2:2) at pD 6.4 and 50 °C was elucidated by a combination of ^{31}P, ^{31}P DOSY and ^{31}P EXSY NMR spectroscopy, demonstrating the potential of these techniques for the analysis of complex reaction mixtures involving polyoxometalates (POMs). ^{31}P and ^{31}P DOSY NMR measured for pure ZrK 2:2 and for the solution containing ZrK 2:2 and ATP at pD 6.4 shows that in the presence of ATP, ZrK 2:2 converts into the more active species ZrK 1:1 and this species is responsible for the hydrolysis of the phosphoanhydride bonds.[1] Two possible parallel reaction pathways were proposed on the basis of the observed reaction intermediates and final products. The ^{31}P spectrum of a mixture of 20.0 mM ATP and 3.0 mM ZrK 2:2 at pD 6.4 measured immediately after sample preparation, shows the formation of a complex I1A and I1B between ATP and POM. During the course of the hydrolytic reaction at pD 6.4 and 50 °C, various products including adenosine diphosphate (ADP), adenosine monophosphate (AMP), pyrophosphate (PP) and phosphate (P) were detected. In addition, several intermediate species representing ADP/ZrK 1:1 (I2), AMP/ZrK 1:1 (I3), P/ZrK 1:1 (I4) and PP/ZrK 1:1 (I5) complexes were also identified. ^{31}P EXSY NMR spectra evidenced slow exchange between ATP and I1A, ADP and I2, and PP and I5.



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C15

Structural Changes of a Vanadium Polyoxoanion: A Mystery.

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Abstract

A very recent paper by the group of Guang-Gang Gao[7] attracted our interest owing to an alluring geometric re-arrangement of a lesser known $[V_{12}O_{34}]^{10-}$ isopolyanion all taking place within the confinement of a decahedral $[Ag(^tBuS)_{20}]^{10+}$ counter-ion. This $C_{2h} \rightarrow D_{3d}$ structural change is induced by pH lowering accompanied by a change in chromaticity (green to yellow). The latter property is a consequence of the 3*d*-3*d* transitions of the doubly reduced POM [V(V)/V(IV)]. While the C_{2h} isomer has a well-defined crystal structure, and holds a fair similarity to another one that has been previously[8] found, the proposed D_{3d} structure is novel and is plagued by considerable disorder in the oxygen atom positions. Our intent is to provide some computational insight into these isopolyanions with a special emphasis on the structural nature of this elusive D_{3d} structure.

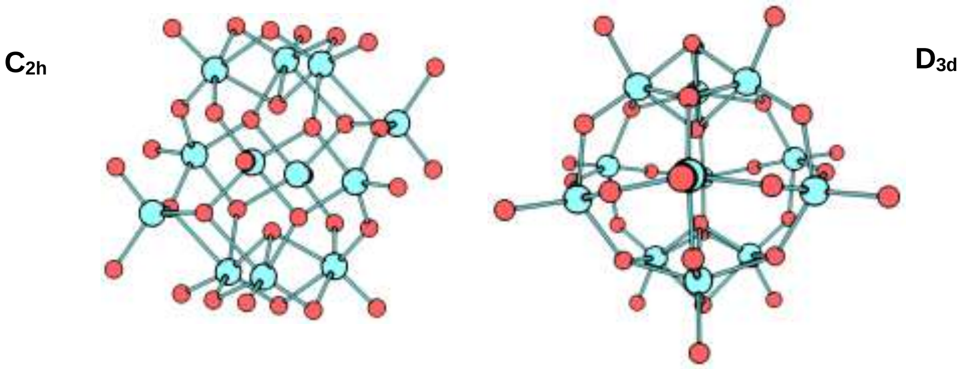

Figure 1 - Inner core of the reported $[V_{12}O_{34}][Ag(^tBuS)_{20}]$ ion pair isomers: the C_{2h} structure (left) and the D_{3d} structure (right).

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Thermo-Structural Studies in Vanadate–Metalorganic Hybrid Compounds: Dynamic vs. Robust Open-Framework Materials

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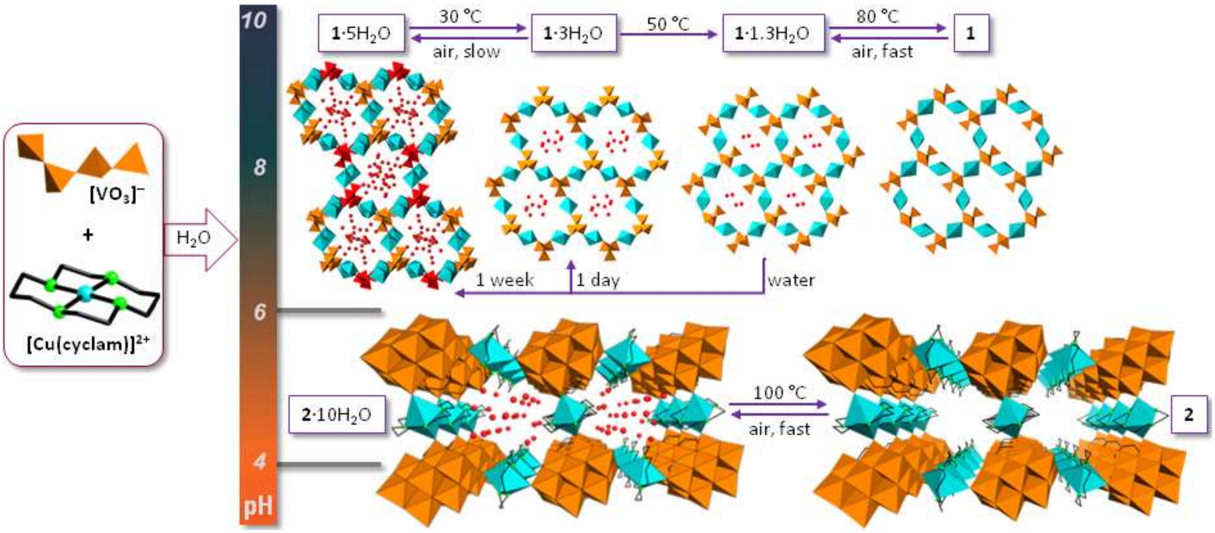
Abstract

The reaction of $[VO_3]^-$ anions and $[Cu(cyclam)]^{2+}$ complex cations (cyclam = 1,4,8,11-tetraazacyclotetradecane) results in the $[\{Cu(cyclam)\}(VO_3)_2]\cdot 5H_2O$ ($\mathbf{1}\cdot 5H_2O$) and $[Cu(cyclam)][\{Cu(cyclam)\}_2(V_{10}O_{28})]\cdot 10H_2O$ ($\mathbf{2}\cdot 10H_2O$) open-framework materials at pH > 6 and pH 4–6, respectively.[9] The dynamic structure of $\mathbf{1}\cdot 5H_2O$ undergoes up to three sequential and reversible single-crystal-to-single-crystal transitions triggered by thermal dehydration to lead to the anhydrous form **1** through the intermediate phases $\mathbf{1}\cdot 3H_2O$ and $\mathbf{1}\cdot 1.3H_2O$. In contrast, the robust POMOF-like supramolecular structure of $\mathbf{2}\cdot 10H_2O$ remains virtually unaltered upon thermal evacuation of guest solvent molecules, resulting in the anhydrous phase **2** with accessible micropores.



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[a]BCMaterials, Spain. [b]Universidad Católica de Ávila, Spain. [c]Universidad de Alicante, Spain.

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Following the Reaction of Heteroanions inside a $\{W_{18}O_{56}\}$ Polyoxometalate Nanocage by NMR Spectroscopy and Mass Spectrometry

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Abstract

The electron transfer and storage features of redox-active pyramidal heteroanions incorporated Dawson-like $\{W_{18}\}$ clusters showed promising applications in the field of flash memory devices.[1] However, we are yet to obtain direct spectroscopic evidence demonstrating the reactivity of heteroanions "trapped" within a molecular metal oxide POM nanocage.[2] By incorporating $\{HPO_3\}$ into a POM cage, a new type of Dawson-like cluster, $[W_{18}O_{56}(HP^{III}O_3)_2(H_2O)_2]^{8-}$, was isolated. We studied the reactivity of the cluster using both solution state NMR spectroscopy and mass spectrometry. These techniques show the cluster undergoes a structural rearrangement in solution whereby the $\{HPO_3\}$ moieties dimerise to form a weakly interacting $(O_3PH\cdots HPO_3)$ moiety. In the crystalline state, a temperature-dependent intramolecular redox reaction and structural rearrangement from $[W_{18}O_{56}(HPO_3)_2(H_2O)_2]^{8-}$ to $[W_{18}O_{54}(PO_4)_2]^{4-}$ occurs.

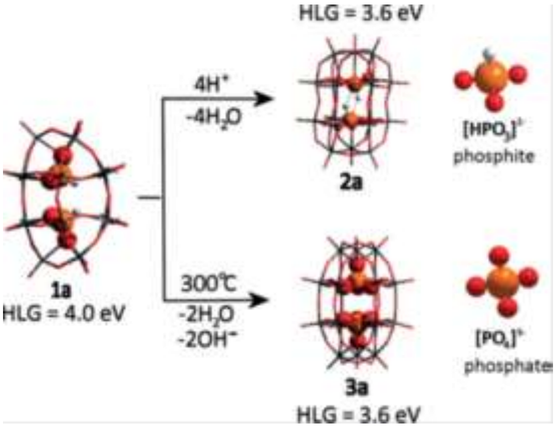

Figure 1. Structure of "Trojan horse"-type cluster $[W_{18}O_{56}(HP^{III}O_3)_2(H_2O)_2]^{8-}$ (**1 a**) in solution, peanut-like Dawson cluster $[W_{18}O_{54}(HP^{III}O_3)_2]^{4-}$ (**2 a**; proposed structure), and the classic Wells–Dawson cluster $[W_{18}O_{54}(P^{V}O_4)_2]^{6-}$ (**3 a**). Energy values for the HOMO–LUMO gap (HLG) for compounds **1 a**, **2 a**, and **3 a** are given in eV. Atom colors: O=red; P=orange; W=dark gray; H=light gray.

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C18

STM Investigation of the Co-assembly Behaviour of POMs clusters with Host Molecule 1,3,5-tris(10-carboxydecyloxy)benzene (TCDB)

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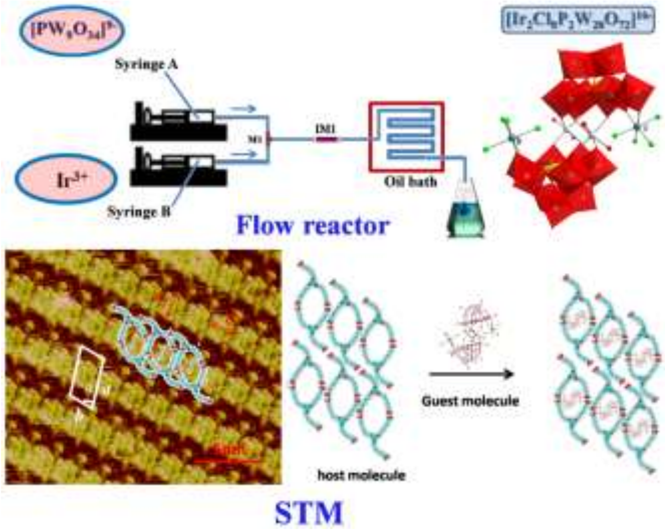
Abstract

Compared with the reported $K_{14}[(IrCl_4)KP_2W_{20}O_{72}]$ compound,[1] efficient synthesis of the iridium(III)-containing polytungstate cluster $K_{12}Na_2H_2[Ir_2Cl_8P_2W_{20}O_{72}]\cdot 37H_2O$ (**1**) has been achieved by using a continuous flow apparatus.[2] On the Highly Oriented Pyrolytic Graphite (HOPG) surface, 1,3,5-Tris(10-carboxydecyloxy) benzene (TCDB)[3] has been used as the two dimensional host networks to co-assemble cluster **1**, the surface behaviour has been observed by Scanning Tunneling Microscope (STM) technique. ''S''-shaped of **1** has been observed, indicated that the cluster could be accommodated in the cavity which formed by two TCDB host molecules, leading to a TCDB/cluster binary structure.



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From giant chalcoPOMs to giant polyoxoniobates

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Abstract

Hybrid polyoxometalate-cluster complexes represent a relatively new and potentially rich area of polyoxometalate (POM) chemistry. The robust molybdenum sulfide cluster building blocks ($\{Mo_2O_2(\mu\text{-}S)_2\}^{2+}$ and $\{Mo_3S_4\}^{4+}$) and various POM fragments combine together producing a wealth of remarkable nano-sized architectures [1]. Our studies of coordination in $WO_4^{2-}/SeO_3^{2-}/\{Mo_2O_2S_2\}^{2+}$ systems as function of pH values and concentration found formation either of a giant box-like W_{76} (Fig.1, left) or a wheel-like W_{42} polyoxometalates at different pH values.

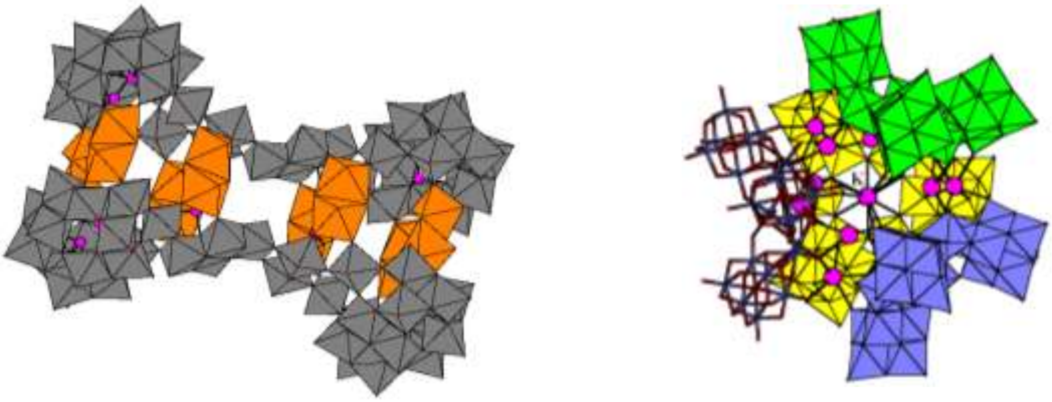

Fig. 1.

Polyoxoniobates can form hybrid nanoscopic aggregates with alkali metals and complexes with transition metals in the basic solutions [2]. In this research we focused on the problem of cation depending formation of $[Nb_{24}O_{72}]^{24-}$ and preparation of $Cu/\{Nb_7O_{22}\}$ complexes.

The work was supported by COST STSM program (COST-STSM-ECOST-STSM-CM1203-101015-062506) and Russian Science Foundation (RScF 14-13-00645).

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Chiral Dodecanuclear Palladium(II)-Thio Cluster: Synthesis, Structure, and Formation Mechanism

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Polynuclear cage complexes have attracted significant interest in the past decades due to their intriguing variety of architectures and properties.[1] In particular, the synthesis and characterization of chiral metal clusters are of great importance by virtue of their potential applications in asymmetric catalysis, chiral separation, and biochemistry.[2] Developing simple and reliable strategies to construct chiral discrete polynuclear metal-oxo/thio clusters still remains a challenge and needs to be further explored. As the square-planar coordinated d^8 noble metal ion Pd^{II} exhibits structure-directing capability during the self-assembly process, it is expected that the combination of Pd^{II} ions and *L*-cysteine (*L*-Cys) ligands may produce chiral clusters with attractive structures and properties. Herein, we report on the synthesis, structure and formation mechanism of a novel chiral dodecapalladium(II) cluster. The chiral cluster presents a dimeric assembly $LaPd_{12}(L\text{-Cys})_{24}$ (**1**), with two hexanuclear $\{Pd_6(L\text{-Cys})_{12}\}$ subunits connected by a decacoordinated La^{III} ion via La-O bonds. To the best of our knowledge, compound **1** represents the largest discrete chiral 4*d*-4*f* palladium(II)-thio cluster. The cluster **1** was characterized by single crystal XRD, TGA, IR, UV-Vis, CD and ^{13}C NMR spectroscopy. The dimerization process of **1** was studied by ESI-MS and DFT calculations, which suggests that $Pd_6(L\text{-Cys})_{12}$ is an essential intermediate in the self-assembly of **1**.

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Designing novel $SiO_2@NH_2$-$PMo_{11}V$ based nanomaterials with reversible photo- and thermochromic properties

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Abstract

In the last decades, photochromic inorganic compounds such as transition metal oxides and polyoxometalates (POMs) have been attracting much attention due to their potential applications in optical switches, solar energy conversion and optical memories devices[1]. Among POM properties, the capacity to reversibly exchange a large number of electrons with marginal structural rearrangement producing the mixed-valence coloured species (heteropolyblues or heteropolybrowns) makes them suitable building blocks for the development of novel photochromic materials[2,3].

In this work, tetra-butylammonium salt of the vanadium-substituted phosphomolybdate $[PMo_{11}VO_{40}]^{4-}$ ($PMo_{11}V$) was immobilized onto amino-functionalized silica nanoparticles. The resulting materials were characterized in terms of morphology, particle size and chemical composition by several techniques, which proved the success of the silica amino-functionalization and POMs immobilization processes. The reversible photo- and thermochromic properties in the solid state were evaluated by UV-Vis spectroscopy and colorimetry.

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Nanometer-Size Heterometallic Polyoxometalate Clusters for Functional Applications

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Abstract

Transition metal oxide species are being used for variety of applications such as data storage devices, magnetic sensors, lithium ion batteries, photolysis, catalysis and nanomaterials.[1a] Polyoxometalates (POMs) are discrete molecular forms of metal oxides that can be further functionalized by incorporation of virtually any metal ion and thus are excellent substrates for the fabrication of functionalized composite materials.[1b] The ability of a lacunary POM to act as a super ligand allows not only the encapsulation or incorporation of single TM species, but also for aggregates of these.[1c,d] As part of our effort to encapsulate 3d and 4f transition metal centers within POM framework, we have successfully made giant polyanions $[\{(GeW_9O_{34})_2Dy_3(OH)_3\}_6\{Co^{II}_2Dy_3(OH)_6(OH_2)_6\}_4]^{56-}$ **$(Dy_{30}Co_8W_{108})$**[1e] and $[\{(GeW_9O_{34})_2Sm^{III}_3(\mu\text{-}OH)_3(H_2O)\}_{12}\{Co^{II}_2Sm^{III}_3(\mu_3\text{-}OH)_6(OH_2)_6\}_8(CoO_2)_2]^{110-}$ **$(Sm_{60}Co_{18}W_{216})$**. These hybrids interestingly represent a new structural topology in POM chemistry and are the first to incorporate two different 3d–4f and 4f coordination cluster assemblies within same POM framework. **$(Sm_{60}Co_{18}W_{216})$** is by far the largest discrete heterometallic polyoxotungstate with largest number of 4f metal centers.

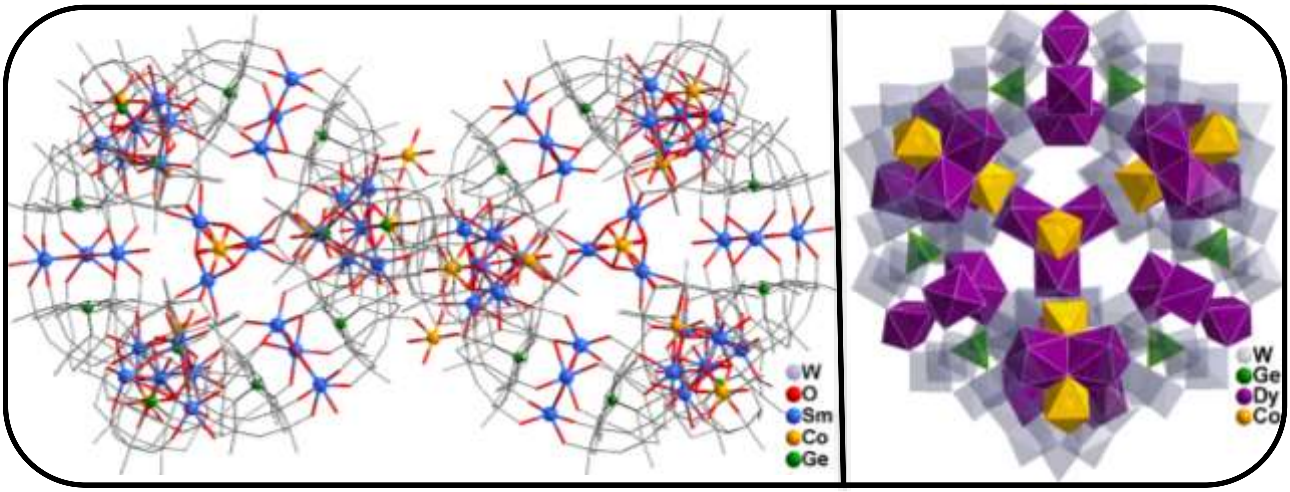

Figure. (Left) **$\{Sm_{60}Co_{18}W_{216}\}$** (right) **$\{Dy_{30}Co_8W_{108}\}$**

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Construction of larger polyoxometalates using the cubane-containing $[Co_4(OH)_3(H_2O)_6(PW_9O_{34})]^{4-}$ as a building block

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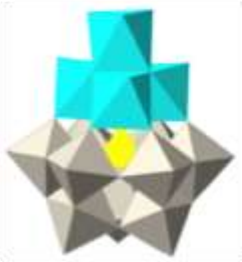
Abstract

The synthesis of new cobalt-containing polyoxometalates is interesting because they represent an excellent opportunity to conduct detailed studies on the magnetic exchange interactions in Co^{2+} clusters.[1,2] Recently, we reported several new cobalt clusters with cubane-type topologies encapsulated in trivacant polyoxometalate ligands and studied their magnetic properties.[2] We have found that one of them ($[Co_4(OH)_3(H_2O)_6(PW_9O_{34})]^{4-}$, **1**) is versatile enough to be used as a building block for the construction of larger polyoxometalates, thanks to its ability to substitute the water molecules coordinated to the cobalt atoms of the cubane cluster by oxygen atoms of another (different) polyoxometalates (see figure). In this communication, the structures and magnetic properties of the compounds obtained following this strategy will be shown.



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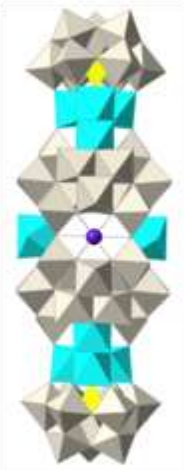

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Zr(IV)-Substituted Polyoxometalates as a novel class of artificial proteases: Catalytic and molecular interaction studies

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Abstract

Selective cleavage of proteins is one of the most important procedures in analytical biochemistry and biotechnology applications, frequently used for protein structure/function/folding analysis, protein engineering, and target-specific protein-cleaving drug design.[10] This is, however, a challenging task. Commonly used natural proteases are expensive, operate only in a narrow temperature and pH range, often suffer from self-digestion and often have limited selectivity. Therefore, new, efficient, and selective cleaving agents that are sufficiently active at non-denaturing pH and temperature conditions are highly needed.

In the search for new artificial peptidases, Zr(IV) was incorporated into lacunary polyoxometalate frameworks (POMs) to form metal-substituted polyoxometalates, which have been intensively investigated in our research group for the hydrolysis of peptides and proteins.[11] In this study, reactivity of a series of Zr(IV)-substituted POMs towards the hydrolysis of peptide bonds in dipepties and proteins as well as the interaction between POMs and the substrates were investigated. The cleavage was purely hydrolytic, occurred under mildly acidic or physiological pH, and was selective. The interaction was evidenced by several spectroscopic techniques such as ^{1}H NMR, ^{13}C NMR, ^{31}P NMR, circular dichroism (CD), tryptophan fluorescence, and UV-Vis spectroscopies.

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C25

A decacobalt(II) cluster with triple-sandwich structure obtained by reductive hydrolysis of a pentacobalt(II/III), Weakley-type, polyoxometalate

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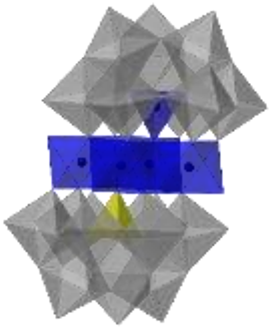
Abstract

In the last years, our group has obtained and studied several Co^{2+}-containing polyoxometalates (POMs) for their interest in molecular magnetism.[1, 2] In this work, we report the synthesis and characterization of a topologically unprecedented deca-Co^{2+}-containing POM, $[Co_{10}(OH)_4(H_2O)_2(W_7O_{26})_2(PW_9O_{34})_2]^{22-}$ (**2**), which has been obtained by partial reductive hydrolysis of a penta-$Co^{2+/3+}$-containing asymmetric sandwich POM, $[Co_5(H_2O)_2(W_9O_{34})(PW_9O_{34})]^{12-}$ (**1**). While **1** is a Weakley-type single-layered sandwich polyoxoanion, **2** can be considered as a S-shaped, triple-layered sandwich POM, made up of two capping $[PW_9O_{34}]^{9-}$ units and two bridging $[W_7O_{26}]^{10-}$ units which assemble to encapsulate a decacobalt core comprising octahedral and tetrahedral Co^{2+} ions. **1** and **2** have been characterized by different physical methods, including single-crystal XRD, mass spectrometry, cyclic voltammetry, ^{31}P-NMR and magnetic measurements.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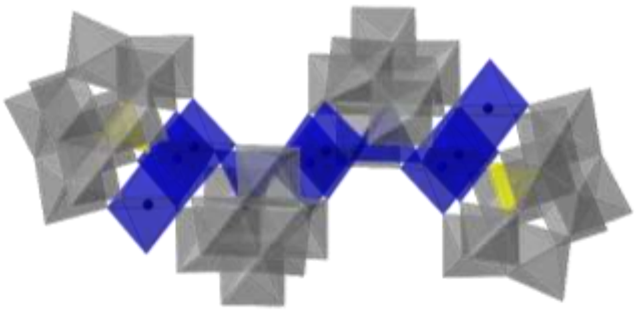
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Self-Templating and *in-situ* Assembly of a Cubic Cluster-of Cluster Architectures based on a $\{Mo_{24}Fe_{12}\}$ Inorganic Macrocycle

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Abstract

Anion templated self-assembly has emerged as a highly effective synthetic approach to construct a wide range of finite and infinite supramolecular architectures.[1] In this regard, some gigantic POMs clusters have been built *via* the templation of smaller POMs such as Keggin-type $\{PMo_{12}\}$, Dawson-type $\{P_2W_{18}\}$, and $\{Mo_{36}\}$ anions.[2-4] We are particularly interested in developing POM-templated self-assembly as general approach to fabricate highly complex POMs, with the aim of understanding the underlying principle of POMs-templated host-guest system. To this end, a series of $\{Mo_{24}Fe_{12}\}$ macrocycles featuring supramolecular tetrahedron architecture are discovered *via* POMs-templated self-assembly. The anionic templates could be either produced *in-situ* or added directly as an external director. The mechanism of formation is revealed for this host-guest system and transformation between macrocycles is realized by template-exchange. More importantly, the concept of using $\{Mo_{24}Fe_{12}\}$ as confined reaction vessel is achieved by *in-situ* generation of uncapped Dawson $\{Mo_{12}(HPO_3)_2\}$ within macrocycle.

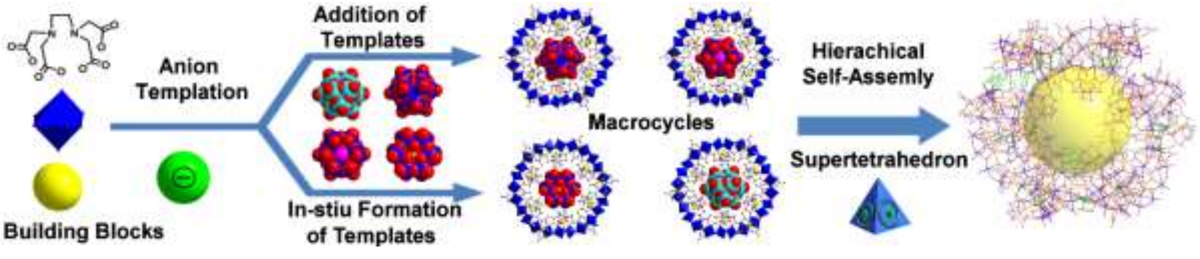

Figure 1. Anion-templated hierarchical self-assembly of $\{Mo_{24}Fe_{12}\}$ macrocycles.

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Polyoxometalate-Protected Gold-Nanoparticle Building Units

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Abstract

This talk will cover recent findings concerning metal-oxide clusters (POMs) as protecting ligands for metal(0) nanoparticle (NP) structural building units. In 2008, we used cryogenic transmission electron spectroscopy (cryo-TEM) to obtain the first direct images of POM-monolayer shells on metal(0) NPs in water [1-3]. We subsequently discovered that the POM ligand shells provided remarkable control over reactions with alkanethiols in water, leading to investigations of alkanethiolate ligand-shell formation on gold NPs [4], and the development of Au NPs as structural building units, first demonstrated via the insertion of thiols with cationic endgroups into POM ligand shells to give dipolar (Janus) patchy NPs that assemble into micron-sized polymers [5]. We now report the use of POM-ligand shells to control the hydrophobic assembly of colloidal analogs of Au-NP superlattices, in which spherical 200-nm diameter assemblies each serve as hosts for more than two million molecular guests [6]. In addition, POM-controlled reactions have led to amphiphilic Au NPs that form micelles in water, and then, as nano-scale analogous of molecular surfactants, solubilize nano-droplets of liquid xylene [7]. More generally, these developments provide new options for achieving a long-standing goal in nano-science: the use of ligand-shell protected metal(0) NPs as structural building units.

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Polyoxometalate Nano Hair Clips: From Carbon Nanostructures recognition to applications

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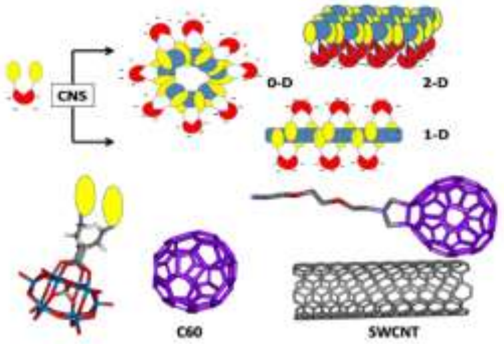
Abstract

Organized supramolecular structures are of great importance in natural systems and work as inspiration for the scientists in the construction of artificial multifunctionalities. Supramolecular architectures allow the construction of composite/hybrid materials from the discrete molecules through non covalent interactions. Polyoxometalates (POMs) are distinguished polyanionic metal-oxygen clusters. These molecules attract a lot of interest due to their large domains of applications.[1] In particular, the preparation of hybrid POMs, in which the inorganic domain is integrated with different organic moieties or molecules, represents a major strategy to develop novel supramolecular structures and molecular materials with unique structural and electronic behavior.[1-4] In particular, divacant Keggin-type polyoxotungstates can be selectively decorated with a tweezer-like motifs which can be exploited to bind hetero-transition metals or neutral guests.[5-7]

Herein, we present a few examples of divacant Keggin-type polyoxotungstates bisfunctionalized with aromatic molecules, and their use for the design of hybrid materials with Carbon Nanostructures (Fullerenes and Carbon Nanotubes).



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Preparation of a nanocomposite composed of polyoxometalates and cationized graphene for aqueous supercapacitors

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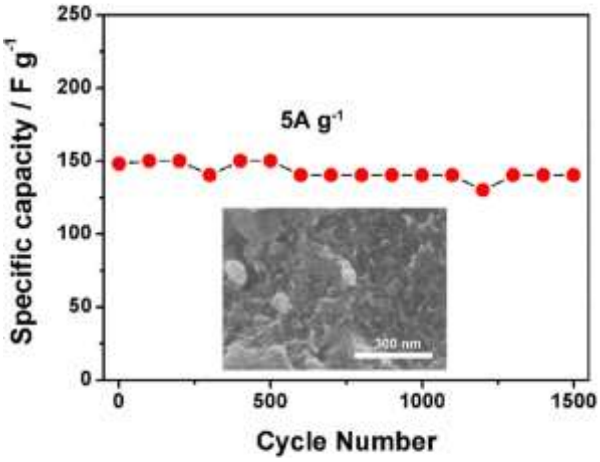
Abstract

Polyoxometalates (POMs) are an excellent candidate for making composite materials for energy storage due to the unique electrochemical reactivity. Herein, we report on the fabrication of a composite based on POMs modified by poly(dimethyl diallyl) ammonium (PDDA) functionalized graphene (PDDA-RGO), through a facile, *in situ* hydrothermal method. The cationic polyelectrolyte PDDA was employed as linkers to adsorb both RGO and POMs through electrostatic interactions. The obtained POM-PDDA-RGO composite exhibits a homogeneous honeycomb-like porous structure, indicating a fast ion transport and short ion diffusion pathways. In a typical two-electrode symmetric system, the supercapacitors show good rate capacity and cycle stability in the acidic electrolyte solution (1 M H_2SO_4).



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X-ray and Neutron Scattering Study of the Formation of Core-Shell Type Polyoxometalates

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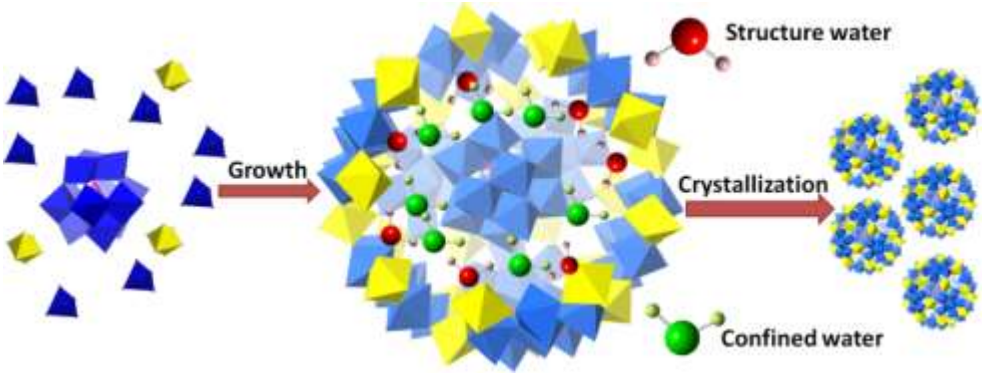
Abstract

A typical type of core-shell polyoxometalates can be obtained through the Keggin-type polyoxometalate-templated growth of a layer of spherical shell structure of {$Mo_{72}Fe_{30}$}. Small angle X-ray scattering is used to study the structural features and stability of the core-shell structures in aqueous solutions. Time-resolved small angle X-ray scattering is applied to monitor the synthetic reactions and a three-stage formation mechanism is proposed to describe the synthesis of the core-shell polyoxometalates based on the monitoring results. New protocols have been developed by fitting the X-ray data with customed physical models, which provide more convincing, objective, and completed data interpretation. Quasi-elastic and inelastic neutron scattering are used to probe the dynamics of water molecules in the core-shell structures and two different types of water molecules, the confined and structured water, are observed. These water molecules play an important role in bridging core and shell structures and stabilizing the cluster structures.[1]



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Polyoxoniobates containing Noble Metals

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Abstract

The chemistry of polyoxometalates (POM) is a rapidly growing area of modern coordination chemistry. One of the emerging research lines in this field is chemistry of polyoxoniobates and tantalates, which offer various chemical challenges like generation of pentagonal building blocks, nanosized catalysts for water splitting (WS)[2] etc.

We have found that reaction of $[(C_6H_6)RuCl_2]_2$ and $Na_8[Ta_6O_{19}]$ gives, depending on the reagent ratio, two new hybrid organometallic-POM complexes – $Na_{10}[\{(C_6H_6)RuTa_6O_{18}\}_2(\mu\text{-}O)]\cdot 39.4H_2O$ (1:1 ratio) and Na_4(*trans*-$[\{(C_6H_6)Ru\}_2Ta_6O_{19}]\cdot 20H_2O$ (2:1 ratio). In both cases the half-sandwich fragments $\{(C_6H_6)Ru\}^{2+}$ are coordinated as additional vertices to the $\{Ta_3(\mu_2\text{-}O)_3\}$ triangles.

Reactions between $[M_6O_{19}]^{8-}$ (M = Nb, Ta) and $[Cp^*RhCl_2]_2$ gives *trans*-$[\{Cp^*Rh\}_2M_6O_{19}]^{4-}$, that was isolated and characterized with different methods as $K_4[\{Cp^*Rh\}_2Nb_6O_{19}]\cdot 20H_2O$ and $Cs_4[\{Cp^*Rh\}_2Ta_6O_{19}]\cdot 18H_2O$ correspondingly. Grafting of $\{Cp^*Ir\}^{2+}$ fragments onto $[M_6O_{19}]^{8-}$ (M = Nb, Ta) gives 1:1 and *trans*-1:2 complexes, which were fully characterized as sodium salts. These reactions also can be transferred to the recently started by us water solution chemistry of $[(OH)TeNb_5O_{18}]^{6-}$. We isolated and characterized *trans*-$[\{Cp^*M\}_2(OH)TeNb_5O_{18}]^{2-}$ (M = Rh, Ir). Te atom locates in the central M_4 plane that was found from x-ray and NMR.

In the present work complexation of platinum(IV) with $[Nb_6O_{19}]^{8-}$ was studied with different techniques. Thus, a dimeric complex $Cs_2K_{10}[Nb_6O_{19}\{Pt(OH)_2\}]_2\cdot 13H_2O$ when hexaniobate $[Nb_6O_{19}]^8$ reacts with Pt(IV) in 1:1 molar ratio, while increasing of the Pt/Nb_6 ratio to 2:1 gives crystals of a sandwich-type $Cs_2K_{10}[(Nb_6O_{19})_2Pt]\cdot 18H_2O$ complex.

The work was supported by Russian Science Foundation (RScF 14-13-00645).

Introducing Thallium in Polyoxometalate Chemistry

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The aqueous solution chemistry of Tl^{3+} is dominated by a high tendency for hydrolysis, resulting in the formation of Tl^{3+}-hydroxo complexes. Contrary to the lighter metal ions of group 13, Tl^{3+} does not form polynuclear hydroxo-complexes,[1] and compounds with more than one Tl atom are known mainly in organo-thallium chemistry.[2] Tl-containing compounds are widely used in electrical, medical, and even glass manufacturing industries[3].

The area of Tl-containing POMs is barely investigated. Some thallium salts of di-, para- and metatungstates have been prepared by conventional methods.[4] In 1953, Magneli[5] first described the structure of hexagonal tungsten bronze A_xWO_3, and later and Shivahare[4] (1964) and Bierstedt[6] (1965) isolated $Tl_{0.3}WO_3$ and $Tl_2W_4O_{13}$, respectively. These compounds are extended tungsten oxides and hence not classified as POMs. To date no structurally characterized discrete Tl-containing polyanion has been reported.

We were inspired by the above work, and thus decided to attempt incorporating thallium in a POM cluster. Herein we report the synthesis and structure of a thallium(III)-containing tungstosilicate. We also used Tl NMR and ESI-MS to study the solution stability of this compound.

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Polyoxometalate electro-oxidation of sulphur-containing molecules

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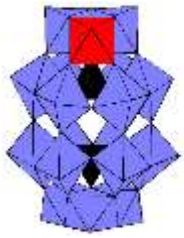
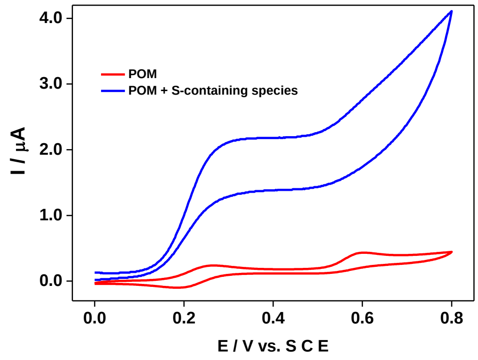
Abstract

Polyoxometalates (POMs) have a very rich and varied electrochemistry due to: i) their capacity to exchange several electrons in a reversible way with no structure changes; ii) the possibility to modulate their redox properties upon changing the nature of the transition metals in their scaffold. Hence, a set of carefully chosen POMs known to be electro-active in a particular potential range may turn out to be particularly effective electro-catalysts of certain redox reactions of interest.[1,2] This is the case for some Re- and V-substituted tungstic Dawson-type POMs which behave as electro-catalysts for the oxidation of sulphur-containing organic molecules. This work aims at mimicking oxidative stress processes involving biological relevant species such as cysteine and at unravelling their respective reaction mechanisms.[3] Classic electrochemical techniques are used, namely cyclic voltammetry and controlled potential coulometry, and the study is complemented by the estimation of the values of several physico-chemical parameters using a simulation software.[4]

L-Cys





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P04

Organic Photosensitizer attached Polyoxometalate as Catalyst for Reduction of CO_2

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Abstract

Catalytic recycling of carbon dioxide (CO_2) to fuels (such as; CO, HCOOH, etc.) is an important goal to satisfy the increasing demand of fossil fuel. The purpose of this project is to replace noble-metal photo catalyst with earth abundant transition metal catalyst and find the convenient sacrificial e^- donor for photocatalytic conversation CO_2 to fuels. A common idea in this area is to use transition-metal complex as a photocatalyst with added photosensitizer.[1] The role polyoxometalate (POM) for reduction of CO_2 has not been studied extensively so far.[2] Herein photosensitizer attached Anderson type POM,[3] $[Mn^{III}Mo^{VI}O_{24}]^{9-}$ has been investigated for catalytic reduction of CO_2.

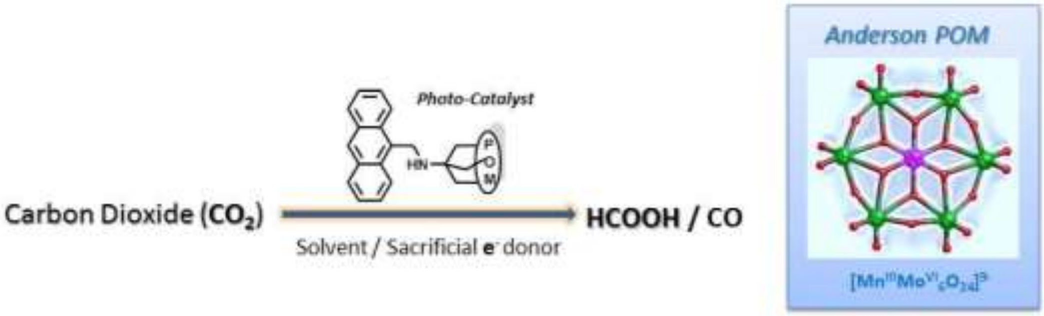

Figure: Photosensitizer attached Anderson type POM as photocatalyst for reduction of CO_2

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Exploration of Synergy between Ruthenium Nanoparticles and Polyoxometalates for Biomass Conversion Catalysis

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Abstract

With growing concerns about diminishing petroleum reserves, energy demand, environmental pollution and greenhouse gas emission, the development of new methodologies and catalysts for the transformation of biomass and biomass derived compounds into biofuel components has attracted worldwide attention. The hydrogenation of biomass-derived 5-hydroxymethylfurfural (HMF) to 2,5-dimethylfuran (DMF) is a key reaction in upgrading biomass-derived furanic compounds into platform molecules toward the production of chemicals and liquid transportation fuels.[1] Polyoxometalates (POMs), such as phosphotungstic acid ($H_3PW_{12}O_{40}$), may possess acidity even stronger than H_2SO_4.[2,3] There is evidence that Ru^0 nanoparticles and POMs can act in tandem for (i) activation of H_2 and (ii) creation of strong Brønsted acidity,[4] but POM-stabilised Ru nanoparticles are difficult to recover and re-cycle. Water-tolerant polymer-immobilised ionic liquid phase (PIILP) supports have therefore been used as scaffolds upon which to immobilize Ru^0/POM nanoparticles to give it bifunctional catalysts for the hydrogenation of HMF.

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Iridium-Containing Polyoxometalates with Unique double Anderson-Evans Structure

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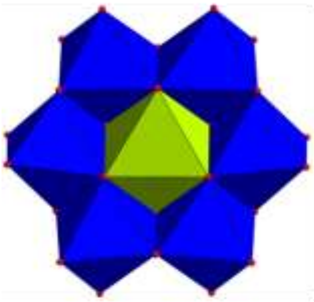
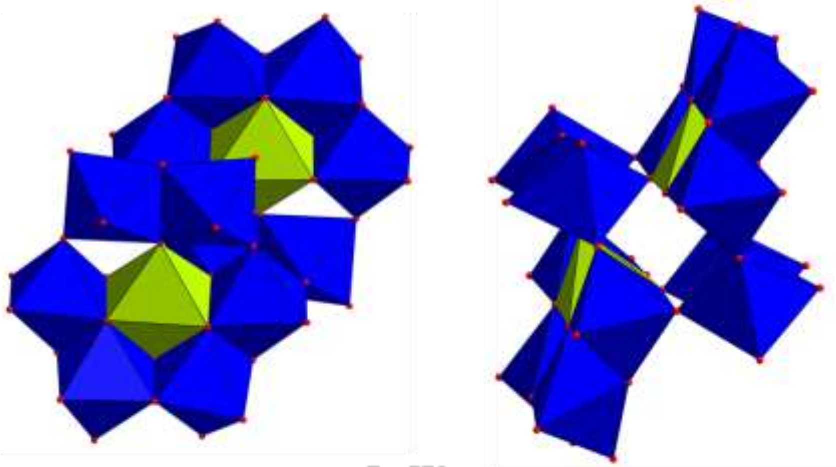
Abstract

Iridium-containing polyoxometalates attract considerable attention as potential catalysts for numerous chemical oxidation processes ranging from low-temperature O_2-based oxidation to water splitting. Recently we have reported the Ir^{IV} centered polyoxotungstate $[Ir^{IV}W_6O_{24}]^{8-}$ (**IrW_6**) with Anderson-Evans structure, exhibiting interesting electrochemical activity.[1] During further investigation of the solution behavior of **IrW_6** polyanions we have found the it can undergo structural rearrangements and dimerization leading to $[H_xIr_2W_6O_{48}]^{z-}$ (**Ir_2W_{12}**) species of the unique structural archetype. Electrochemical and EPR behavior of the novel polyanions will be also presented.



IrW_6



Ir_2W_{12}

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Non-aqueous Synthesis and Electrochemical Behaviour of Post-Transition Metal Substituted Keggin Polyoxotungstates

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Mono-substituted Keggin polyoxometalates (POMs) have been studied greatly because of their broad applications in fields such as catalysis, energy systems, nanoscience and medicine.[1-3] Electrochemical studies on these POMs have mostly been on aqueous solutions[4-6] with only a few reports in non-aqueous media.[7-9] Our non-aqueous studies of POMs aim to develop an understanding of their reactivity and redox chemistry in order to tune their properties for applications in catalysis and molecular nanoscience. Five mono-substituted Keggin POMs, $[ClMPW_{11}O_{39}]^{n-}$, (M = Sn^{4+}, Bi^{3+}, Sb^{3+}) and $[MPW_{11}O_{39}]^{5-}$, (M = Sn^{2+}, Pb^{2+}) were prepared *via* non-aqueous reactions between $[NaPW_{11}O_{39}]^{6-}$ and metal halides. Products were characterized by CHN microanalysis, FTIR, UV, Multinuclear (^{31}P, ^{119}Sn, ^{207}Pb and ^{183}W) NMR spectroscopy and cyclic voltammetry. An electrochemical study in MeCN showed that the tungstate cage of lacunary POM (PW_{11}) was more readily reduced than that for heterometallic POMs $[ClMPW_{11}O_{39}]^{n-}$, (M = Sn^{4+}, Bi^{3+}, Sb^{3+}) and $[MPW_{11}O_{39}]^{5-}$, (M = Sn^{2+}, Pb^{2+}). No heterometal redox processes were observed for $[ClSnPW_{11}O_{39}]^{4-}$ and $[PbPW_{11}O_{39}]^{5-}$, while redox waves for Sn^{2+}/Sn^{4+}, Sb^{3+}/Sb^{0} and Bi^{3+}/Bi^{0} were observed for $[SnPW_{11}O_{39}]^{5-}$, $[ClSbPW_{11}O_{39}]^{5-}$ and $[ClBiPW_{11}O_{39}]^{5-}$ respectively within the potential range studied.

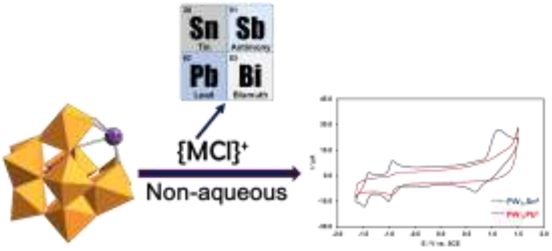

Figure 1: Non-aqueous synthesis and CVs of $[MPW_{11}O_{39}]^{5-}$ (M = Sn^{2+}, Pb^{2+})

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DFT Study of Polyoxometalates on Gold Surfaces: from Structure to Catalysis

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Abstract

Adsorption of polyoxometalates (POMs) on surfaces and nanoparticles provides a new platform for their application in catalysis. The first goal of our work is to obtain general strategies for the modelling of POMs on gold surfaces with periodic DFT methods. Polyanions such as $[Mo_6O_{19}]^{2-}$, $[PMo_{12}O_{40}]^{3-}$ on Au(111) and highly charged $[PW_{11}O_{39}]^{7-}$ on Au(100) were to identify the main factors that are necessary to take into account in the modeling of POMs deposited onto a gold surface.[12] The incorporation of counterions has revealed to be strictly necessary to have reasonable electronic properties even if implicit solvent is used in the modeling. We also report preliminary calculations on the oxidation mechanism of CO catalyzed by $[PMo_{12}O_{40}]^{3-}$ over a gold surface.[13] Initially, the adsorbed water is dissociated heterolytically by transferring one proton to the POM and leaving hydroxyl on the Au surface; a process that requires to overcome a barrier of only 12.7 kcal·mol^{-1}, much lower than for pure Au (> 40 kcal·mol^{-1}). The step corresponding to CO oxidation is also assisted by the POM, which allows to reduce significantly the energy barrier for the global process.

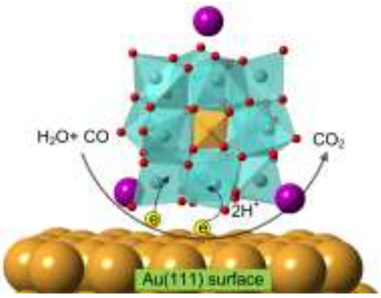

Figure1. Reaction schemic of CO oxidation on $K_3PMo_{12}O_{40}$/Au(111) surface.

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P09

Polyoxometalates as Pincer Ligands?

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^{17}O-enriched samples of tetra-*n*-butylammonium (TBA) salts of Lindqvist-type anions $[(MeO)TiW_5O_{18}]^{3-}$ were prepared *via* non-aqueous hydrolysis from $WO(OMe)_4$, $(^nBu_4N)_2WO_4$ and $Ti(OMe)_4$ and ^{17}O-enriched water.[1]

Hydrolysis of $(TBA)_3[(MeO)TiW_5O_{18}]$ at room temperature was shown to be much slower than that of the tin analogue $(TBA)_3[(MeO)SnW_5O_{18}]$; FTIR spectroscopy showed evidence for $[(HO)TiW_5O_{18}]^{3-}$ with ν(OH) at 3673 cm^{-1}, in addition to $(TBA)_6[(\mu\text{-}O)(TiW_5O_{18})_2]$, which is the ultimate product upon heating.

^{17}O NMR studies of the protonation of $(TBA)_6[(\mu\text{-}O)(TiW_5O_{18})_2]$ with HBF_4 are consistent with the formation of $[(\mu\text{-}O)\{TiW_5O_{18}H\}_2]^{4-}$ and the DMSO adduct has been characterised by X-ray crystallography (Fig. 1). Characteristic upfield shifts for TiOW peaks upon protonation are also observed upon addition of other electrophiles. In reactions involving $CsAuCl_4$, $SnCl_4$ or Me_2SnCl_2, ^{17}O NMR indicated a decrease in overall charge and the upfield shifts of TiOW peaks suggest binding to these sites.[2] This raises the intriguing possibility that polyoxometalates might act as non-innocent “pincer” ligands, and DFT calculations indicate that the hypothetical structure for the gold complex $[(\mu\text{-}O)\{TiW_5O_{18}H\}_2(AuCl)]^{4-}$ shown in Fig. 2 should be stable.

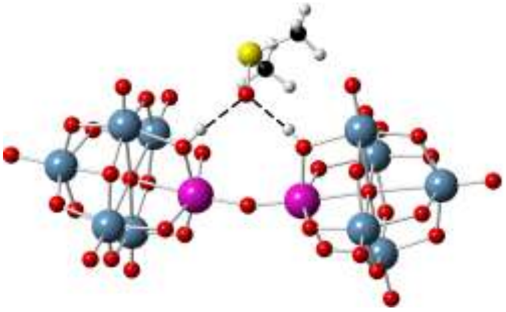

Fig.1

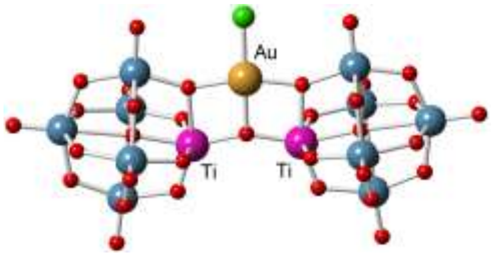

Fig.2

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Sequential Single–Crystal–to–Single–Crystal Transformations in a 3D Covalent Heptatungstate-based Hybrid with Permanent Porosity

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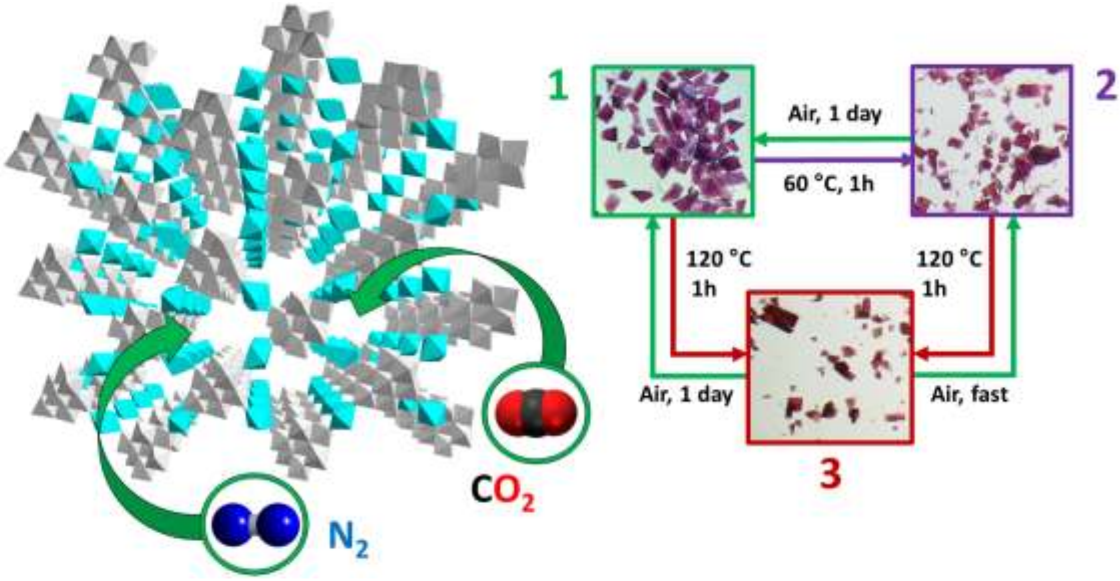
Abstract

As one of the scarce examples of hybrid compounds based on a paratungstate A species, the extended $[\{Cu(cyclam)\}_6(W_7O_{24})_2]\cdot31H_2O$ (**1**) (cyclam = 1,4,8,11–tetraazacyclotetradecane) has been synthetized and fully characterized. This porous covalent structure changes its dimensionality from an initial 3D assembly to a layered arrangement $[\{Cu(cyclam)\}_6(W_7O_{24})_2]\cdot24H_2O$ (**2**) due to the rotation of alternate layers and consequent migration of a Cu atom to an adjacent $\{WO_6\}$ octahedron as evidenced by a thermally triggered single–crystal–to–single–crystal transformation upon partial dehydration. Total dehydration leads to the anhydrous $[\{Cu(cyclam)\}_6(W_7O_{24})_2]$ (**3**) which undergoes further structural changes associated to the simultaneous migration of Cu atoms and cluster rearrangement within layers. While **1** and **2** show a single type of channels, the rearrangement of the heptatungstate clusters in **3** resulted in the generation of two types of channels with slightly different sizes. The permanent porosity of **1** and its thermal derivatives was confirmed by gas adsorption measurements and such properties were evaluated.



P11

Synthesis of a Series of Tuneable Polyoxometalates for Water Oxidation

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Abstract

During a collaborative STSM (Short Term Scientific Mission) between the School of Chemistry of Glasgow University and ICIQ in Tarragona funded by the COST action we have been able to synthesise a series of molybdenum and tungsten compounds based on the known $\{Co_4(PW_9)_2\}$[1] which is a catalyst for water oxidation.[2] Herein we report the electrochemical properties that this compounds show and how the incorporation of molybdenum into the structure has modified the water splitting properties of the original compound. In this work we use the modified molybdenum doped compound (in different ratios of Mo:W) as a heterogeneous water oxidation catalyst.

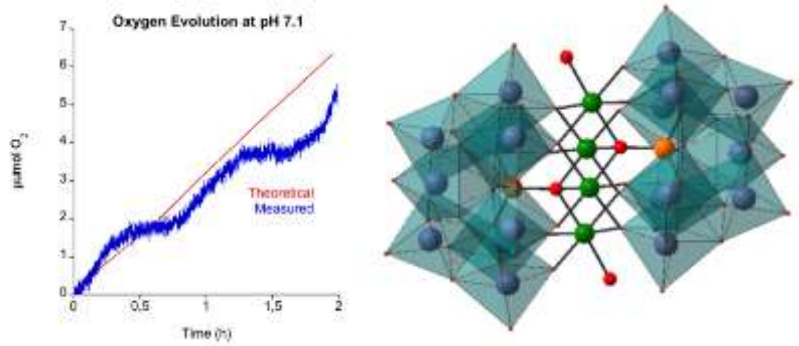

Figure 1. (left). Graph showing the O_2 evolution for the molybdenum doped $\{Co_4(PW_xMo_y)_2\}$ at 1.4V. (right). Polyhedral and ball and stick representation of $\{Co_4(PW_xMo_y)_2\}$, cobalt green spheres, oxygen red spheres, phosphorus orange spheres, WO_6/MoO_6 teal polyhedra

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Computational insight into photochemical H_2 evolution by an iridium (III)-photosensitized polyoxotungstate

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The efficient conversion of solar light into fuels, such as H_2, by a photochemical process is a highly interesting topic and still a scientific and technological challenge after decades of research. In the case of environmentally friendly photochemical reactions, it is established that H_2 evolution relies on the formation of a photoinduced electronic charge separation with a suitable lifetime to permit further electron transfer from a sacrificial agent. In addition, the catalyst has to be able to use these photogenerated charges to produce the chemical fuel as a major reaction outcome. One of the greatest challenges is the integration, in a single molecular framework, of individual subunits able to bring together all these events. In the search for innovative materials for the photochemical production of fuels, polyoxometalates (POMs) have attracted the attention of several research groups due to their unmatched chemical and structural versatility. Artero, Izzet and co-workers [1] showed that a covalent Ir(III)-photosensitized POM in the presence of a sacrificial reducing agent leads to highly efficient photoreduction of the POM. Moreover, the system is able to generate photocatalytic hydrogen under visible light without a significant loss of performance over one week of continuous photolysis. Herein we present a DFT study establishing the reaction mechanism for the process reported in [1] and the identification of the species formed during the stepwise H_2 evolution reaction. Crucial electrochemical aspects of the reaction are also discussed. In our opinion, these theoretical results may shed some light into the intricate process of photoinduced H_2 evolution.

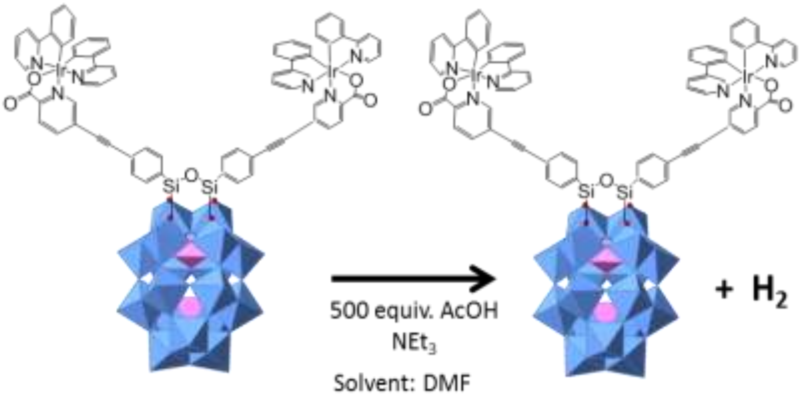

Figure 1. Iridium (III)-photosensitizied polyoxotungstate. The blue polyhedral framework corresponds to the mono-lacunary α_2-$[P_2W_{17}O_{61}]^{10-}$ structure, where each octahedron is a WO_6 unit

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P13

Preparation of a nanocomposite composed of polyoxometalates and cationized graphene for aqueous supercapacitors

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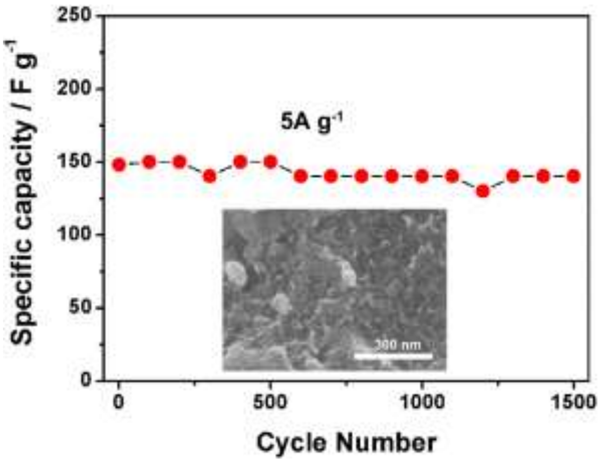
Abstract

Polyoxometalates (POMs) are an excellent candidate for making composite materials for energy storage due to the unique electrochemical reactivity. Herein, we report on the fabrication of a composite based on POMs modified by poly(dimethyl diallyl) ammonium (PDDA) functionalized graphene (PDDA-RGO), through a facile, *in situ* hydrothermal method. The cationic polyelectrolyte PDDA was employed as linkers to adsorb both RGO and POMs through electrostatic interactions. The obtained POM-PDDA-RGO composite exhibits a homogeneous honeycomb-like porous structure, indicating a fast ion transport and short ion diffusion pathways. In a typical two-electrode symmetric system, the supercapacitors show good rate capacity and cycle stability in the acidic electrolyte solution (1 M H_2SO_4).



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Polyoxometalates for Redox Flow Batteries

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Abstract

Redox Flow Batteries (RFBs) are one of the few options to store electrochemical energy efficiently on a large scale. Energy storage is a requirement for the grid integration of intermittent renewable energy sources such as wind and solar power. However, the only commercially mature RFB, the All-Vanadium RFB (VBR) suffers from low energy- and low power-density[1,2]. These shortcomings are direct consequences of physical and chemical properties of the employed dissolved transition metal ions.

We report our efforts to improve the energy- and power-density of RFBs by employing polyoxometalates (POMs) as nanosized electron carriers. Electrochemical properties of various anolyte and catholyte compositions featuring POMs were determined in a three-electrode setup. Suitable electrolytes were further tested in a laboratory scale flow-battery. Figures of merit are high solubility, high cell-voltage, low reaction overpotential and stability in multiple oxidation states. Also various electrodes, including carbon papers and carbon felts, thermally treated and untreated, were compared considering the overall cell resistance and kinetic interactions with the electrolytes. Results from extended cycling experiments indicate that POM electrolytes can drastically enhance energy- and power-density of RFBs.

To simplify battery operation, POMs were prepared in reduced forms and electrochemically and spectroscopically investigated. Furthermore the permeation of POMs through commercially available cation exchange membranes was tested and compared to cross-over of the ferric/ferrous redox couple.

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Decavanadate Based Hetero-metallic Inorganic-organic Hybrids as Highly Active Electrocatalysts for Hydrogen Evolution

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Abstract

Polyoxometalates (POMs), a class of redox facile metal-oxy anion clusters, are steadily emerging as efficient, cheap, precious-metal-free electrocatalysts for hydrogen evolution reaction (HER).[14,15,16] We have synthesized, three decavandate ($V_{10}O_{28}^{6-}$) based supramolecular inorganic-organic hybrids (**1**, **2** and **3**) using different ligands (2,2'-bipyridine: **1**, 4-amino pyridine: **2**, and ethylene diamine: **3**) and Cu as the secondary transition metal (only in **1** and **2**) for electrocatalytic HER applications. Single crystal analysis revealed that in **1**, the Cu atom (octahedrally coordinated) was directly linked to the decavanadate unit while in **2**, Cu formed a separate octahedral complex that was linked to the decavanadate unit only through non-covalent interactions. Hybrid **3** exhibited excellent HER activity as cathode in acidic media with an onset overpotential of only 120 mV, charge transfer resistance (R_{CT}) as low as 580 Ω at -160 mV (vs RHE) and the catalytic current density of 10 $mA.cm^{-2}$ was reached at an overpotential of 260 mV. The Tafel slope, 121 $mV.dec^{-1}$, indicates that Volmer step is the r.d.s for HER in case of **3**. The comparative activity order followed as 3>2>1, where the onset overpotential for **2** and **1** were at 180 mV and 280 mV respectively. The trend suggests that there is a synergistic effect of both the transition metals (Cu and V) towards the catalysts' HER activity. Theoretical and experimental studies are going on to understand the role of structural, electronic and conductive properties of the three hybrids in determining their relative HER activity.

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POM-based materials as electrocatalysts for proton and NOx reduction

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Abstract

Polyoxometalates (POMs) are highly functionalizable soluble molecular entities exhibiting a large variety of properties ranging from catalysis to magnetism. By association with organic linkers or metal complexes POMs can serve as building blocks in extended hybrid frameworks. In this contribution, two types of POM based materials with electrocatalytic properties will be described. The first ones are POM-based Metal Organic Frameworks (called POMOFs)[17] formed by connection of capped ε-Keggin units with organic linkers. The second are heteroanionic materials based on copper clusters, bisphosphonates and POM units.[18] The synthetic routes and the electrocatalytic properties of the POMOFs and heteroanionic materials for proton and NOx reduction, respectively, will be presented.

Figure 1: Representation of a POMOF material

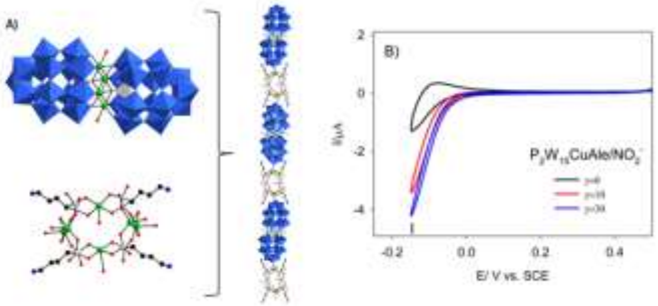

Figure 2: A) Representation of the POM unit, the copper cluster and the resulting heteroanionic material.
B) Electrocatalysis of NO_2^- reduction

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Polyoxometalate-based Inorganic/Organic Hybrids

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Abstract

Organically modified polyoxometalates (POMs) can be designed by the combination of POMs with suitable organic groups.[1a,b,c,d] The synergic effects of the Inorganic/Organic hybrids may bring interesting properties to the resultant materials. As a part of our research to develop POM-based Inorganic/Organic hybrids we have synthesized $[(Al(OH)_3Mo_6O_{18})_2(O\text{-}CH_2)_3C\text{-}HN\text{-}CH\text{-}C_6H_4\text{-}CH\text{-}HN\text{-}C(CH_2\text{-}O)_3]^{-6}$ **(1)** and $[(AlMo_6O_{18})((O\text{-}CH_2)_3C\text{-}CH_2\text{-}O\text{-}CH_2\text{-}C\text{-}(CH_2\text{-}OH)_3)_2]^{-3}$ **(2)**. Polyanions **1** and **2** were obtained under hydrothermal conditions by the reaction of Tris-phenyl-Tris and dipentaerythritol with Anderson-Evans POMs, respectively. Polyanion **1** consists of two $\{Al(OH)_3Mo_6O_{18}\}^{3-}$ units which are linked via sixfold deprotonated Tris-phenyl-Tris, whereas **2** is made up of two threefold deprotonated dipentaerythritol which are attached to the POM. The obtained products were characterized by single-crystal X-ray diffraction, FTIR, UV/Vis spectroscopy and TGA.

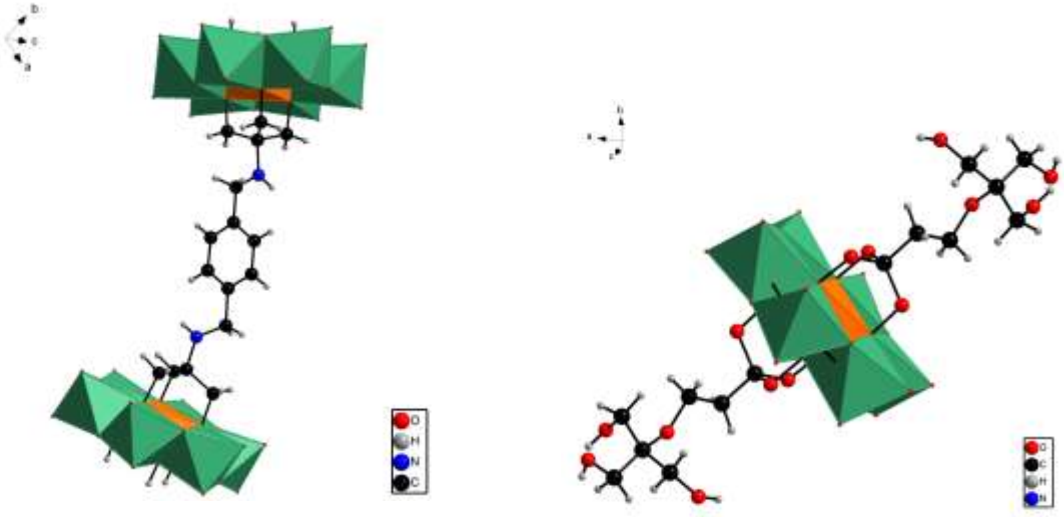

Figure: left: Compound **1** and right: Compound **2**.

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That organic extra something: *in silico* studies on two remarkable organic-polyoxometalate hybrids

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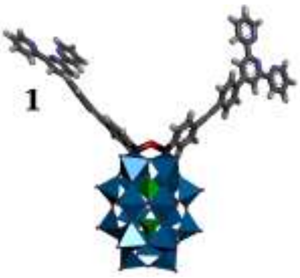
Abstract

In this communication, we present our latest computational studies on two remarkably different organic-polyoxometalate hybrids (OPHs),[19] aiming to support and rationalise their previous meticulous experimental characterisation.[20,21]

OPH **1** ($[P_2W_{17}O_{61}\{O(SiC_{29}H_{18}N_3)_2\}]^{6-}$) is composed of a Dawson anion, whereunto two long alkynyl-phenyl-terpyridine (tpy) arms are attached by means of a siloxane tether.[20] In the presence of Fe(II), **1** self-assembles into oligomeric units $[Fe_x\mathbf{1}_x]^{4x-}$, whose further aggregation is controllable by solvent conditions. Our calculations show that such units may coexist as triangles ($x = 3$) and squares ($x = 4$).

In OPH **2** ($[PW_{11}O_{39}\{Sn(C_{31}H_{23}N_2O_3)\}]^{4-}$), a photosensitive stannyl(IV)-alkynyl-benzospiropyran group is grafted onto a Keggin anion.[21] In this case, we focus on unveiling why **2** is prominently luminescent, whilst its fragments on their own are not.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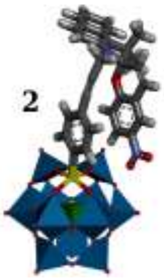
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Regular Pattering of Polyoxometalates on Surfaces

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Abstract

Controlled molecular surface deposition is an important challenge on the way to fabricate molecule-based devices.[1] One possible approach utilizes suitable linking groups (LGs) which can be covalently attached to the surface as well as to the molecules of interest, in our case polyoxoanions, motivated by their features attractive for molecular electronics (e.g. redox versatility, thermodynamic stability), which make them prospective for application in spintronics.[2]

Here we present several 1:2 polyoxometalate (POM) / LG associates (e.g. Fig. 1) which were synthesized and characterized in solid state and in solution as well as the first results on Au surface modification with the POM/LG assemblies (Fig. 2) obtained during an STSM in the group of Prof. Dr. Dominique Vuillaume (Institute of Electronics, Microelectronics and Nanotechnology (IEMN, CNRS, France).

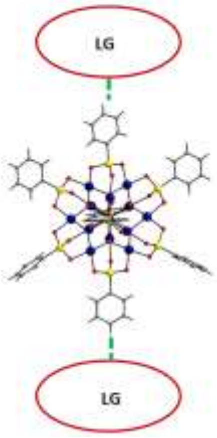

Fig. 1

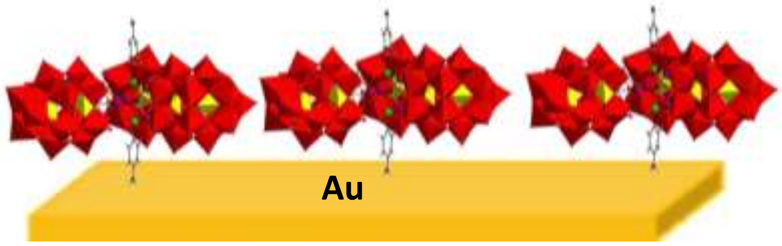

Fig. 2

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P20

Supramolecular Organization of Graphene-anchored Photosynthetic Nano-arrays

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Abstract

There exists a fundamental and technologically important challenge in the solar-fuels research field: How to couple molecular catalysts to photoactive domains and to drive water oxidation catalysis by visible light without the use of applied potential biases or sacrificial reagents. In a collaborative effort between Israeli and Italian research teams, we demonstrate here a new, supramolecular strategy towards achieving this end. Previously, we have visualized the non-specific organization of polyoxometalates (POMs) onto gold nanoparticle (AuNP) surfaces[1]. Furthermore, we found cationic thiols to insert themselves between the POM monolayer and the AuNP surface[2,3]. We now add functionality to this system by incorporating a $Ru_4(\mu\text{-}O)_4(\mu\text{-}OH)_2(H_2O)_4(\gamma\text{-}SiW_{10}O_{36})_2$ POM (**Ru_4POM**) water-oxidation catalyst[4] and then inserting photoactive disulfides, bearing cationic $Ru(bpy)^{3+}$, into the assembly to co-localize catalyst and chromophore (**Figure 1 A,B**). Utilizing graphene's ability to bind gold nanorods,[5] we attach AuNPs to covalently-modified graphene (**Figure 1C**) in a bottom-up post-functionalization scheme to integrate these nano-arrays with electrodes. The goal for these integrated electrodes is to demonstrate visible-light photoelectrochemical water oxidation without the need for sacrificial reagents.

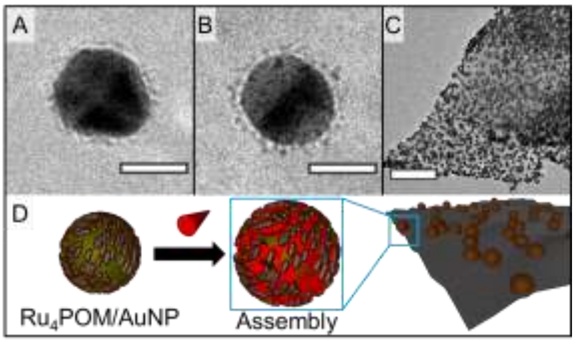

Figure 1: First steps toward a graphene anchored photosynthetic nano-array. Cryogenic transmission electron microscopy images show a AuNP and its **Ru_4POM** monolayer prior to (A) and after (B) insertion of a photoactive sulfide. Scale bars = 10 nm. (C) Conventional transmission electron micrograph of nanoarrays on graphene. Scale bar = 200 nm. (D) Representations of sulfide insertion and AuNP-decorated graphene.

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Structural and magnetic investigations of a mononuclear 4f polyoxometalate family with single molecule magnet behaviour

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Abstract

The story of molecular magnetism begins with the reports by *Sessoli* et *al.*[1] on $[Mn_{12}O_{12}(O_2CMe)_{16}(H_2O)_4]$, $\{Mn_{12}\}$, and the observation of a slow magnetic relaxation process in a molecular material. Over the last two decades the number of reported single molecule magnets (SMMs) did not cease to grow with several examples of 3d, 4f and mixed 3d-4f complexes.[2]

The first mononuclear lanthanide complex $[Ln(W_5O_{18})_2]^{9-}$ (Ln = Ho, Er) with SMM behaviour was published by *Coronado* et *al.* in 2008.[3] After this breakthrough, similar approaches were extended to the Preyssler-type series $[Ln(P_5W_{30}O_{110}]^{12-}$ (Ln = Tb, Dy, Ho, Er, Tm, Yb) and the Keggin-type structure $[Ln(\beta_2\text{-}SiW_{11}O_{39})_2]^{13-}$ (Ln = Dy, Ho, Er, Yb). Up to now, only three types of mononuclear 4f POM complexes exhibiting SMM behaviour have been observed, joining the very short list of published polyoxometalates exhibiting this peculiar magnetic property.

Here, we highlight[4] a new family of mononuclear 4f polyoxometalates with a large variety of lanthanide ions (Ln = Gd, Tb, Dy, Ho, Er, Yb, Eu). The crystal structure of all new POMs was successfully solved and the full magnetic measurements with alternating current (ac) and direct current (dc) have been performed. Preliminary results on the $[Er(\beta_2\text{-}GeW_{11}O_{39})_2]^{13-}$ suggest the presence of SMM behaviour. Moreover, careful studies of the erbium coordination geometry show that the Er^{3+} ion is embedded in a favourable antiprismatic geometry.

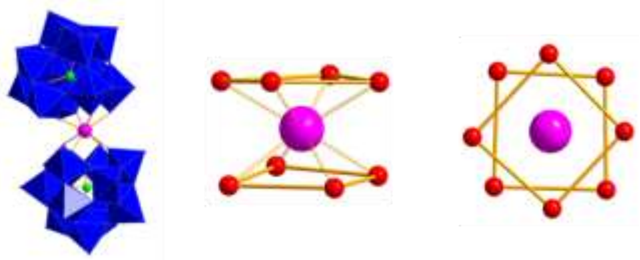

Fig. 1: Ball and stick/polyhedral representation of $[Er(\beta_2\text{-}GeW_{11}O_{39})_2]^{13-}$ and projections showing the Er^{3+} ion square-antiprismatic coordination.

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P22

A novel heteropoly blue based on Dawson-type tungstogermanates: Crystal Structures and Magnetic Properties

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Abstract

Polyoxometalates can be reduced by acception of various numbers of electrons, which is usually named as “heteropoly blues”. Additional electrons in heteropoly blues can influence its coordination environment on the assembly of heteropoly blue-based crystal frameworks. Therefore, heteropoly blues may form crystalline materials with functional properties such as magnetism, photocatalysis and proton conductivity.[1,2] So far, investigation on Keggin-type heteropoly blues has well been documented, and few Dawson-type heteropoly blues have been reported. In particular, the heteropoly blue based on Dawson-tungstogermanates structure remains largely unexplored.

Herein, we initially synthesized a Dawson-tungstogermanates heteropoly blue $Na_2[C_3H_5N_2]_{14}[(Ge_2W_{16}Mo^{V}_2O_{62})_2]\cdot 18H_2O$. The heteropoly blue was fully characterized by elemental analysis, single-crystal X-ray diffraction, IR spectroscopy, diffuse reflectance UV-vis spectroscopy and magnetic measurement. The magnetic investigation indicated the presence of antiferromagnetic interactions in the compound.

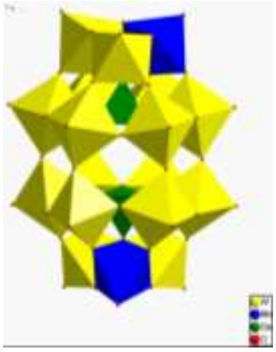

Fig. 1 the crystal structure of the compound

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[2] Wang Y, Xu L, Jiang N, et al, *Cryst Eng Comm.* 2011,13(2): 410-413.

Polyoxometalate Bisphosphonate Complexes: Synthesis, Structure and Activity on Tumor Cell Lines

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Abstract

Bisphosphonates (BPs) are known as antitumoral agents, due to their high affinity to bone minerals. Furthermore, polyoxometalates (POMs) have been studied for a long time for their biological activity. Recently, these organic and inorganic entities have been covalently bounded and the resulting POM/BP hybrids have shown high inhibitory activities against cancer cells, both *in vitro*[22] and *in vivo*. Our current work focuses on synthesizing POM/BP entities incorporating new cations or/and functional groups in order to further enhance their antitumoral activity. First, the incorporation of a second heterometallic element M (M = Mn, Fe) within the POM core has been investigated (Figure 1).[23] Alongside, lipophilic groups have been attached to the Zol ligand (Figure 2). The activity of these new molecules is currently under study.

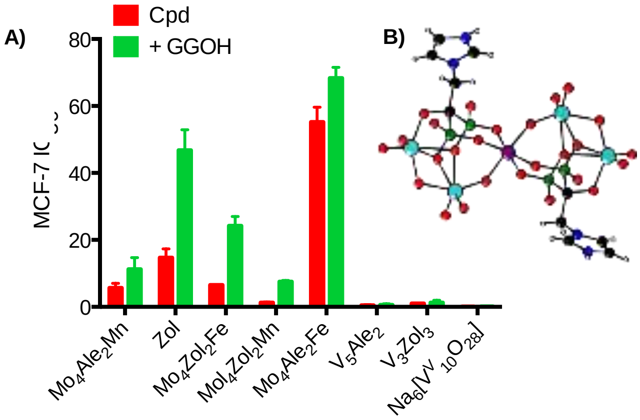

Figure 1: A) Effect of POM/BP inhibitors on human breast cancer

B) Representation of $Mo_4Zol_2M^{n+}$ (M = Mn, Fe)

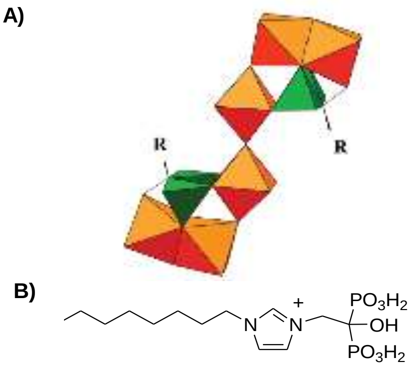

Figure 2: A) Representation of a Mo_6Zol_2 molecule

B) Representation of a lipophilic Zol

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Polyoxometalates complexes of α-Fe_2O_3 cores in water

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Abstract

An unprecedented role for metal-oxide cluster-anions (polyoxometalates, or POMs) as *covalently coordinated inorganic ligands* for individual hematite nanocrystals, gives isolable anionic clusters uniquely positioned between molecular macroanions and traditional colloidal nanoparticles.[1] Sodium salts of α-$PW_{11}O_{39}^{7-}$ anions serve as pentadentate “capping” ligands for complexed Fe(III) ions linked—via their sixth coordination site—to 3-5-nm α-Fe_2O_3 cores. Multiple spectroscopic methods and analytical measurements confirm the presence of POM-capping ligands, [α-$PW_{11}O_{39}$Fe-O-]$^{n-}$, *covalently* bound to the surfaces of the hematite cores. Clear orange solutions of these unique complexes are stable in water over a wide range of *p*H values (2.5-8), which spans the isoelectric point of hematite (*p*H 5.3). Over this entire *p*H range, zeta-potential values (ξ), remain nearly constant, ranging from -33 to -38 mV. Moreover, covalent attachment of the POM anions allows for repeated precipitated (by added salt), and re-dissolution in water. Raman, FTIR, EDS and XPS data show that numerous POMs are associated with each 3-4-nm hematite nanocrystal, and high-resolution TEM, cryogenic-TEM, and HAADF-STEM images clearly reveal the covalently bound POM ligands at the hematite surfaces. As a first step toward reactivity studies (currently underway), differential-pulse voltammetry (DPV) was used to reveal the reversible redox chemistry of the covalently attached POM ligands.

[1] M. Raula, G. Gan Or, M. Saganovich, O. Zeiri, Y. Wang, M. R. Chierotti, R. Gobetto, I. A. Weinstock, *Angew. Chem. Int. Ed*. **2015**, *54*, 12416-12421.

Ion pair tuned cyclic voltammetry behavior of Keggin polyoxometalate quaternary ammonium salts in organic solvents

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Abstract

THE CYCLIC VOLTAMMETRY BEHAVIOR OF KEGGIN POLYOXOMETALATE $[XW_{12}O_{40}]^{(3\text{-}6)-}$ IN ORGANIC SOLVENTS WAS INVESTIGATED. It was observed a logarithm correlation between the solvent's dielectric constant and $E_{1/2}$ disparity in $[PW_{12}O_{40}]^{3-}/[PW_{12}O_{40}]^{4-}$ couple, introduced by *n*-tetraoctyl ammonium and *n*-trioctylmethyl ammonium, $\Delta E_{1/2} = 0.37 - 0.088\ln(\varepsilon + 7.46)$ V. This $\Delta E_{1/2}$ value expanded when POM's surface charge increased, from $[PW_{12}O_{40}]^{3-}$ to $[ZnW_{12}O_{40}]^{6-}$. And in dichloromethane solution or with high POM surface charge, a saturation effect in $\Delta E_{1/2}$ was observed. We ascribe above phenomenons to the solvent-tuned ion pair association-dissociation process. From the diffusion NMR, when solvent's dielectric constant decreased, we observed $[PW_{12}O_{40}]^{3-}$ experienced a transition from free ion to compacted ion pair with quaternary ammnoium. And we also observed that *n*-trioctylmethyl ammonium bond to POM anion more closely than *n*-tetraoctyl ammonium in $[PVW_{12}O_{40}]^{4-}$ ion pair experiment.

The influence of synthesized polyoxometalates on acetylcholinesterase activity

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Abstract

The *in vitro* influence of six polyoxotungstates containing various central atoms and decameric vanadate species $Na_6[V_{10}O_{28}] \times 16H_2O$ on acetylcholinesterase (AChE) activity was investigated. AChE is commercially available and purified from electric eel. The enzyme (0.37 µg proteins) was exposed to the polyxotungstates in the concentration range from 1×10^{-10} to 2×10^{-3} mol/L, during 15 min at 37 °C and pH 7.4. $Na_6[V_{10}O_{28}] \times 16H_2O$ and $Na_{10}[H_2W_{12}O_{42}] \times 27H_2O$ did not markedly affect the enzyme activity, while $K_6[PV_3W_9O_{40}] \times 3H_2O$, $K_6H_2[TiW_{11}CoO_{40}] \times 13H_2O$, $(NH_4)_{14}[NaP_5W_{30}O_{110}] \times 31H_2O$, $K_7[SiV_3W_9O_{40}] \times 10H_2O$, and $K_7[Ti_2PW_{10}O_{40}]$ induced the enzyme inhibition in a concentration-dependent manner. The dependence of the remaining AChE activity, expressed as a percentage of the control enzyme value (obtained without inhibitor), on the inhibitor concentrations fitted a sigmoidal function for all inhibiting polyoxotungstates. Inhibitory power of the investigated compounds was evaluated using IC_{50} values (polyoxotungstate concentration inducing 50% AChE inhibition), which were determined by Hill analysis. $K_7[SiV_3W_9O_{40}] \times 10H_2O$ affected AChE activity with lowest potency ($IC_{50} = 6.9 \times 10^{-4}$ mol/L). $K_6H_2[TiW_{11}CoO_{40}] \times 13H_2O$ and $K_7[Ti_2PW_{10}O_{40}]$ exhibited high affinity toward the enzyme, inducing half-maximum inhibition at micro molar concentrations (1.3×10^{-6} and 1.1×10^{-6} mol/L, respectively), while the same effect was achieved in the presence of about fifty times higher concentration of $K_6[PV_3W_9O_{40}] \times 3H_2O$. Finally, $(NH_4)_{14}[NaP_5W_{30}O_{110}] \times 31H_2O$ was found as the most potent inhibitor of AChE activity ($IC_{50} = 6.6 \times 10^{-7}$ mol/L), and consequently the most promising candidate for the treatment of neurological diseases associated with acetylcholine leakage.

Understanding of formation process of $[Na(PhPO_3)_4(SO_3)_2Mo^V{}_4Mo^{VI}{}_{14}O_{49}]^{5-}$ characterized by ^{31}P-NMR

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Abstract

It has long been known that XO_m^{n-} type oxoanions can act as templates in formation of hetero-polyoxometalates (POM). An important bases which affects the ability of an anion as template is its Lewis basicity. In addition, we recently reported other parameters by which template driven self-assembly was triggered; low oxidation state of Mo and mixing organic solvent.[1] Here, we investigated details of the reaction system by changing organic solvent.

A cluster-**1** (≡$[Na(PhPO_3)_4(SO_3)_2Mo^V{}_4Mo^{VI}{}_{14}O_{49}]^{5-}$) was formed from a reaction of acidified aqueous/acetonitrile mixed solution of molybdate with $PhPO_3^{2-}$ and reductant of $S_2O_4^{2-}$, where self-assembly process was controlled by SO_3^{2-} anion (originated from reductant) as template. By a cooperative effect between SO_3^{2-} and $PhPO_3^{2-}$ (both have similar Lewis basic strength) $PhPO_3^{2-}$ anions are taken into Mo-O cage, but they are only decollated on cluster surface due to bulky phenyl moieties.

Reaction processes to the cluster-**1** were investigated by monitoring it by ^{31}P-NMR where solvent systems are employed by mixture of water and DMF, MeCN, MeOH, EtOH, 2-propanol or acetone.

A solution after 3 days of reaction showed three different ^{31}P-NMR peaks at 21.39 and 21.10, 14.83 ppm, where the last was considered to be originated from cluster-**1**. The spectrum was less dependent on organic solvents. However, cluster-**1** was not observed in 100% water. A peak at 21.44 ppm was observed after dissolving cluster-**1**, showing that cluster-**1** was instable in aqueous media but stabilized by mixing organic solvents.

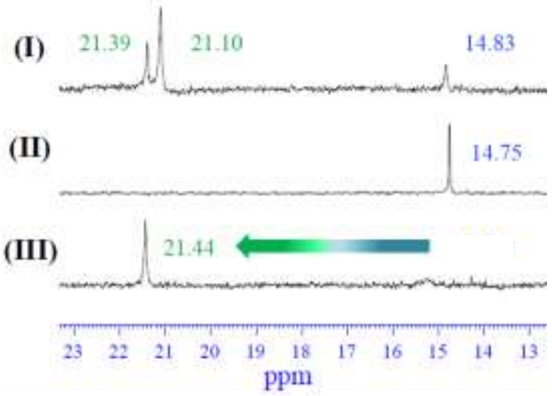

Figure 1. ^{31}P-NMR spectra of reaction solution in water-DMF (5:2) (after 3 days) (I), cluster-**1** in water-DMF (5:2) solution (II), and aqueous solution after dissolving cluster-**1** (III).

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Polyoxometalates as capping ligand for water-soluble ZrO_2 nanoparticles

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In our previous work[1] we have shown an extraordinary assembly of covalently coordinated POM cluster-anions who serve as ligands for water soluble anatase-TiO_2 nanocrystals. POM ligands with tunable redox potentials can provide new options for rationally controlling the reactivity of semiconductor nanocrystals. We herein describe an expansion of our newly developed method to other metal oxide nanoparticles - ZrO_2. Reaction of amorphous ZrO_2 with the 1-nm lacunary Keggin ion, $Na_9PW_{11}O_{39}$ yields an optically clear, water-soluble, nano-sized solution. Different analytical and spectroscopic techniques including NMR, FTIR, DLS, TEM and Cryo-TEM confirm the formation of ca. 30 nm ZrO_2 nanoparticles capped with POM ligands.

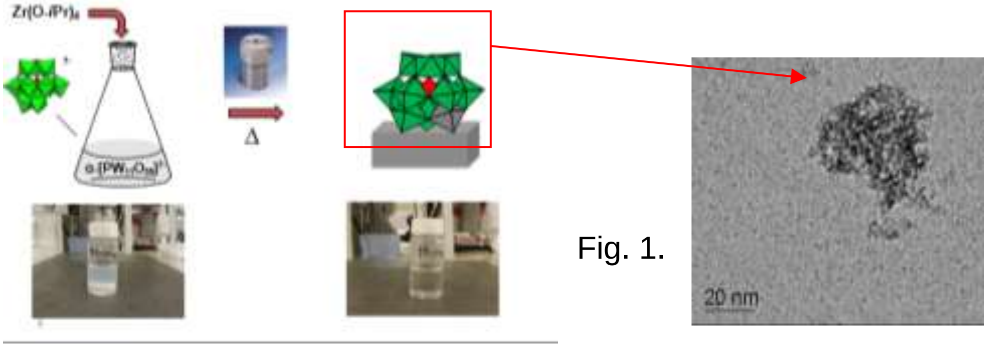

Fig. 1.

Polyoxometalate as capping ligand for water soluble ZrO_2 nanoparticles

1. M. Raula, G. Gan-Or, M. Saganovich, O. Zeiri, Y. Wang, M. R. Chierotti, R. Gobetto I. A. Weinstock, *Angew. Chem. Int. Ed*. 2015, **54**, 12416-1242.

The influence of synthesized polyoxotungstates on Na^+/K^+-ATPase activity

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Abstract

The *in vitro* influence of seven polyoxotungstates containing various central atoms on Na^+/K^+-ATPase activity was investigated. Na^+/K^+-ATPase is commercially available and purified from porcine cerebral cortex. The enzyme was exposed to the polyxotungstates in the concentration range from 1×10^{-10} to 2×10^{-3} mol/L, during 15 min at 37 °C and pH 7.4. All investigated compounds: $K_6[PV_3W_9O_{40}] \times 3H_2O$, $K_6H_2[TiW_{11}CoO_{40}] \times 13H_2O$, $Na_6[TeW_6O_{24}] \times 22H_2O$, $(NH_4)_{14}[NaP_5W_{30}O_{110}] \times 31H_2O$, $Na_{10}[H_2W_{12}O_{42}] \times 27H_2O$, $K_7[SiV_3W_9O_{40}] \times 10H_2O$, and $K_7[Ti_2PW_{10}O_{40}]$ induced the enzyme inhibition in a concentration-dependent manner, but with various potencies. The dependence of the remaining Na^+/K^+-ATPase activity, expressed as a percentage of the control enzyme value (obtained without inhibitor), on the inhibitor concentrations fitted a sigmoidal function for all inhibiting polyoxotungstates. Inhibitory power of the investigated compounds was evaluated using IC_{50} values (polyoxotungstate concentration inducing 50% Na^+/K^+-ATPase inhibition), which were determined by Hill analysis. $Na_6[TeW_6O_{24}] \times 22H_2O$ and $Na_{10}[H_2W_{12}O_{42}] \times 27H_2O$ affected enzyme activity with lowest potency, inducing half-maximum inhibition at millimolar concentrations, while the same effect was achieved in the presence of about hundred times lower concentrations of $(NH_4)_{14}[NaP_5W_{30}O_{110}] \times 31H_2O$, $K_7[SiV_3W_9O_{40}] \times 10H_2O$, and $K_7[Ti_2PW_{10}O_{40}]$. Finally, $K_6[PV_3W_9O_{40}] \times 3H_2O$ and $K_6H_2[TiW_{11}CoO_{40}] \times 13H_2O$ were found as the most potent inhibitors of Na^+/K^+-ATPase activity ($IC_{50} = 3.3 \times 10^{-7}$ mol/L and 1.1×10^{-6} mol/L, respectively). These results suggest potential biological applications of polyoxotungstates as inhibitors of Na^+/K^+-ATPase, the enzyme which has key role in normal functioning of most eukaryotic cells, as well as in development and progression of different cancers.

[1] D.-L. Long, R. Tsunashima and L. Cronin, *Angew. Chem. Int. Ed.*, 2010, **49**, 1736-1758.
[2] L. Cronin, in *Proceedings of the Beilstein Bozen Symposium on Molecular Engineering and Control, ed*. M. Hicks and C. Kettner, Beilstein institut, Berlin 1st edn, 2012, pp.151-166.

Robotics in POM discovery – incorporating automation

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Abstract

Discovery of new polyoxometalates is often performed by systematically varying the concentrations of different reagents in single vessel reactions until the optimum set of parameters are hit upon and the target compound forms.[1] This process can be very labor intensive and subject to human error from small methodological inconsistencies, leading to irreproducible results.[2] To overcome these frustrations, we have created an automated device capable of rapidly scanning the parameter space of a set of reagents and monitoring the crystallization in real time. This allows precise and repeatable measurements of the crystal formation kinetics and correlation between experimental conditions and product yields, whilst minimizing the time required to perform these reactions. This poster presents the hardware and initial findings from an investigation into how addition times and reagent concentrations affect the synthesis of polyoxotungstates.

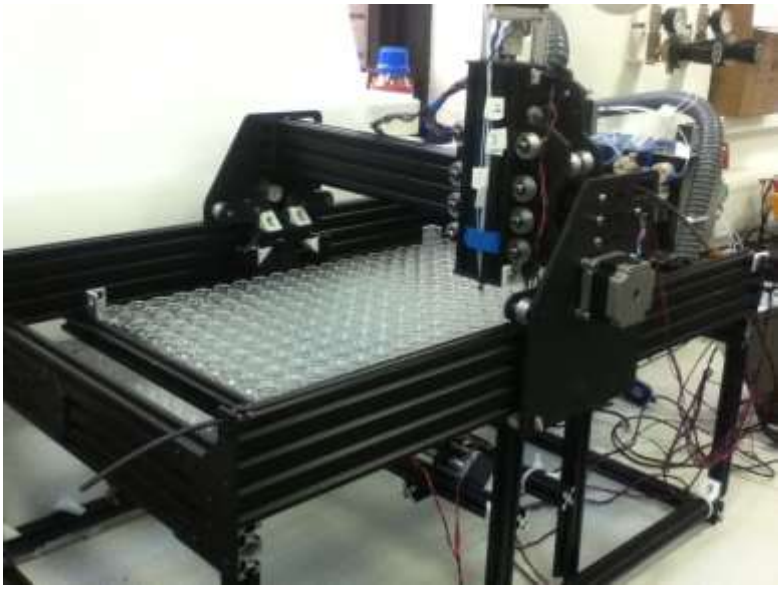

Figure 1. Robotic crystallizer for POM discovery.

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[1] D.-L. Long, R. Tsunashima and L. Cronin, *Angew. Chem. Int. Ed.,* 2010, **49**, 1736-1758.
[2] L. Cronin, in *Proceedings of the Beilstein Bozen Symposium on Molecular Engineering and Control, ed*. M. Hicks and C. Kettner, Beilstein institut, Berlin 1st edn, 2012, pp.151-166.

Chiral Dodecanuclear Palladium(II)-Thio Cluster: Synthesis, Structure, and Formation Mechanism

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Polynuclear cage complexes have attracted significant interest in the past decades due to their intriguing variety of architectures and properties.[1] In particular, the synthesis and characterization of chiral metal clusters are of great importance by virtue of their potential applications in asymmetric catalysis, chiral separation, and biochemistry.[2] Developing simple and reliable strategies to construct chiral discrete polynuclear metal-oxo/thio clusters still remains a challenge and needs to be further explored. As the square-planar coordinated d^8 noble metal ion Pd^{II} exhibits structure-directing capability during the self-assembly process, it is expected that the combination of Pd^{II} ions and *L*-cysteine (*L*-Cys) ligands may produce chiral clusters with attractive structures and properties. Herein, we report on the synthesis, structure and formation mechanism of a novel chiral dodecapalladium(II) cluster. The chiral cluster presents a dimeric assembly $LaPd_{12}(L\text{-Cys})_{24}$ (**1**), with two hexanuclear $\{Pd_6(L\text{-Cys})_{12}\}$ subunits connected by a decacoordinated La^{III} ion via La-O bonds. To the best of our knowledge, compound **1** represents the largest discrete chiral 4*d*-4*f* palladium(II)-thio cluster. The cluster **1** was characterized by single crystal XRD, TGA, IR, UV-Vis, CD and ^{13}C NMR spectroscopy. The dimerization process of **1** was studied by ESI-MS and DFT calculations, which suggests that $Pd_6(L\text{-Cys})_{12}$ is an essential intermediate in the self-assembly of **1**.

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Organoantimony-Containing Polyoxometalates and their Biological Activity

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Polyoxometalates (POMs) are discrete polynuclear metal oxides with a spectacular structural and compositional variety, and a myriad of applications in fundamental and applied science.[1] In particular, organoantimony(III)-containing POMs are by now recognized as bacterial inhibitors with highly tunable bioactivity achieved via the organometallic functionality, coupled with the chemical robustness of the metal-oxo POM support. Our pioneering work has revealed that the number and type of grafted organoantimony(III) species have a strong influence on the resulting bioactivity.[2] However, the number of structurally characterized organoantimony(III)-containing POMs is still small,[2,3] and the detailed mechanism of cell death and the biological targets of such POMs are in general not fully understood yet.[4] Here we present two isostructural tetra-antimony(III)-containing 18-tungsto-2-arsenates(V).

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Towards Stereoselectivity within mixed W/Mo Pentagaonal Building Units in Giant Polyoxometalates

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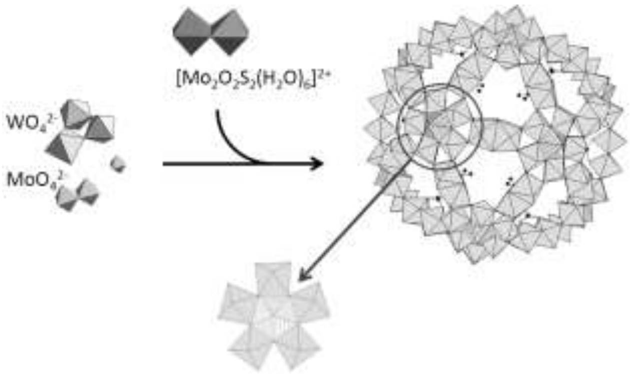
Polyoxometalates (POMs) have already and still gaining a lot of attention due to their unique structures that result in interesting redox, catalytic or optical properties. Among these POMs the Keplerate clusters with the general formula $[(Mo_6O_{21})_{12}(Mo_2O_2E_2)_{30}(Ligand)_{30}(H_2O)_{72}]^{n-}$ (E = O or S) constitute a unique class of highly tunablenanoscopic hollow spherical clusters, comprising 12 metal-oxide pentagonal units connected by 30 linkers spanning an icosidodecahedron structure.[i] Such kind of nanoscopic clusters offers unique possibilities in the field of supramolecular properties, catalysis and materials. For instance, the presence of 20 pores allows transfer of various substrates within the large cavity of the capsule.[ii] Such a process facilitates inner functionalization of the capsule[iii] for promoting catalysis[iv] or chemical reaction[v] under confined reaction. In such a context, the change of the metal-oxo composition of the capsule should allow to tune finely its physical-chemical properties. In this communication, we demonstrate that Keplerate ion can be built on mixed Mo/W pentagonal motifs $\{W(Mo_5)\}$, where the tungsten atoms occupy preferentially the central heptacoordinated position decorated by the five $\{MoO_6\}$ octahedra (see figure below). Such a result means that in such conditions, the polycondensation of the molybdate and tungstate ions correspond to a stereoselective process. Study in solution reveals that the kinetic of the Keplerate formation is directly dictated by the W/Mo ratio while theoretical calculations showed that energy of the isolated pentagons $\{Mo_{(6-x)}W_xO_{21}\}$ are quite independent on the Mo/W distribution. Experimental and theoretical results are quite consistent with kinetic based stereoselectivity. Such a result open new insights for nanoscopic pentagonal-based POM species in general like the giant blue wheel of formula $[Mo_{154}O_{462}(OH)_{14}(H_2O)_{70}]^{14-}$.



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$[Mo_2O_2S_2]^{2+}$ as a Precursor to Chalcogen-infused Molecular Nano-Materials

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Abstract

$[Mo_2O_2S_2]^{2+}$ is an extremely versatile building block that can combine with a variety of templating species to form an incredibly diverse range of structures.[1-3] While much of the work done to explore the potential of this building block has centered around the use of organic templates, recent work in our group has focused more on inorganic species with a number of structures being produced that utilize the selenite (SeO_3^{2-}) anion as a template.[4,5] Present work represents an extension of this by investigating the structures formed with the tellurite (TeO_3^{2-}) anion.

We report the discovery of six compounds, ranging in size from a small $\{Mo_8\}$ ring, to the huge $\{Mo_{72}\}$ cluster that, while still based on the rings we have come to expect from this chemistry, displays topology that has not been observed before. We postulate that the unusual shape and symmetry of these molecules could result in bulk materials with novel morphologies if treated in the correct way, and we present the first results herein

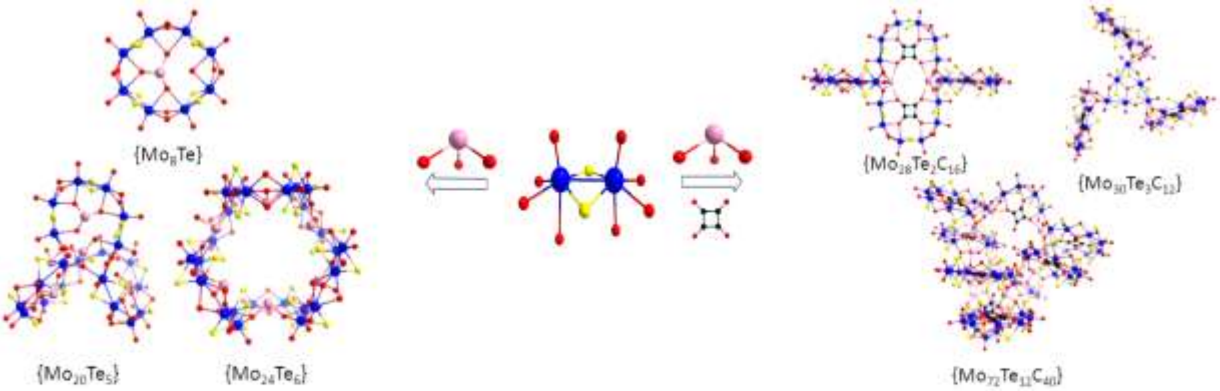

Figure 1. Schematic of the compounds formed with each set of templates

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Organically-Derivatized Polyoxometalates with Enhanced Anticancer Activity

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Abstract

Recently, the medicinal chemistry of POMs is of great interest because various POMs can exhibit effective anticancer, antiviral and antibacterial performances. However, one major obstacle--- POMs being difficult to be effectively modified by biological active molecules, restricts their development and impedes their application in clinical cancer treatment. Herein, we report a series of admantadine modified hexamolybdate, mono-substituted, *cis*-disubstituted and *trans*-disubstituted aliphatic derivatives, which exhibits a better anti-cancer performance on human breast cancer cell MCF-7 than unfunctionalized hexamolybdate and amantadine solely. Moreover, a degradable organoimido derivative of POM (POM-AMB-acy) is developed recently by modifying hexamolybdate with a cleavable organic group, leading to its degradation. Of note, this derivative exhibits favourable pharmacodynamics towards malignant glioma cell U251, the ability to penetrate across blood brain barrier and low toxicity towards PC12 cell. The works presented here indicates that DCC-dehydrating protocol could be an efficient approach to modify POMs with biological activity organic ligands and enhance POMs application in clinical cancer treatment.

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