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ΠΑΝΕΠΙΣΤΗΜΙΟ  
ΠΑΤΡΩΝ  
UNIVERSITY OF PATRAS

## *Sixth North America - Greece - Cyprus Workshop on Paramagnetic Materials*

**Athens, 3-6 June 2015**



## **PROGRAM AND BOOK OF ABSTRACTS**

Sponsored by



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KLOTHAKIS ELEFTHERIOS & Co  
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## **International Organizing Committee**

### *North America*

Professor George Christou, Chemistry Department, University of Florida, USA

### *Greece*

Dr. Georgios Papavassiliou, Institute of Nanoscience and Nanotechnology, NCSR Demokritos, Greece

Professor Spyros P. Perlepes, Chemistry Department, University of Patras, Greece

### *Cyprus*

Assoc. Professor Anastasios J. Tasiopoulos, Chemistry Department, University of Cyprus, Cyprus

## **Local Organizing Committee**

Dr. Georgios Papavassiliou, INN NCSR Demokritos, Greece

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Dr. Vassilis Psycharis, INN NCSR Demokritos, Greece

Dr. Catherine Raptopoulou, INN NCSR Demokritos, Greece

Dr. Georgios Mitrikas, INN NCSR Demokritos, Greece

## **ABOUT ATHENS**

Athens, named after the goddess Athena who was its protector, is famous as the cradle of democracy and one of the foundations of western culture and civilization. The city experienced its 'Golden Age' in the 5th century BC, the time of Pericles, Plato, Aristotle and many many other household names of western thought. This period also bequeathed us the architectural treasures of the Parthenon, the Erechtheion and many other masterpieces.

Today, the city of Athen's glorious past and rich, often turbulent, history can be seen through the major archaeological sites, museums, and attractions scattered throughout the city, coupled with the infrastructure and vibrant life of a modern European city.

## **ACROPOLIS MUSEUM**

The Acropolis Museum houses the findings from the Acropolis of Athens archaeological site. The museum was built to house the objects found on the sacred rock of the Acropolis, covering a wide period from the Mycenaean, to the Roman, to Early Christian Athens. The museum is located on the south side of the Acropolis, less than 300 meters from the Parthenon. The main entrance of the building is located on Dionysiou Areopagitou St. between Makrygiannis Chatzichristou St. and Mitseon St.



## **LOCATION AND TIME**

The Workshop will be held from June 3 to June 6, 2015, at the Acropolis Museum in Athens. The lecture theatre is located within the museum. The museum complex hosts conference facilities as well as a restaurant, cafe, and museum shop.

## REGISTRATION

### Registration desk

The registration desk will be open from Wednesday, June 3 through Saturday June 6, 2015, from 08:15 to 11:00 a.m. each day. There is no registration fee for participants.

## TRAVEL INFORMATION

The Acropolis Museum lies on the archaeological site of Makrygianni, in Plaka, the old historical neighborhood of Athens. It is easily accessible by mass transportation and taxi.

- By taxi: the taxi queue is right outside the arrival level of the airport next to door 3. (There is a fixed fee for carriage from the airport to downtown Athens.)
- By express bus: the express bus X95 will take you in about 45 minutes to its final stop on the south side of Syntagma Square.
- By metro: take metro line 3 - Athens International Airport to Syntagma Station, and then metro line 2 to Acropolis Station.



### Useful telephone numbers:

G. Papavassiliou (mobile phone) (+30693) 6531367

## **SCIENTIFIC PROGRAM**

All presentations will be oral (15 and 30 minutes including discussion). Computer-screen projection (for Power-Point) will be available. The timetable given in the following pages may be subjected to small alterations.

### **Abstract booklet**

The abstract booklet, which includes the final program, can be downloaded at <http://inn.demokritos.gr/Conferences/NAGC15/home.html>. A limited number of hard copies can be requested.

## **SOCIAL PROGRAM**

### **Reception**

The reception (welcome party) will take place, on Tuesday June 2, 2015. The place and time will be announced. All registered persons (participants and accompanying members) are cordially invited.

### **Official Dinner**

The official dinner of the Workshop will take place on Thursday June 3, 2015. A supplement fee is required.

## **GENERAL REMARKS**

### **Climate**

At the beginning of June the weather in Greece is usually hot and dry. The average daytime temperatures lie between 25-30°C, and at night, slightly cooler. The lecture room is air-conditioned.

### **Acknowledgements**

The Organizers wish to thank NCSR "Demokritos", University of Florida, and Klothakis Eleftherios & Co - ANELIS Analytical Environmental Life Industrial Sciences for financial support.

## TIMETABLE NAGC 2015    3-6 June 2015

Time\Day	Wednesday 3	Thursday 4	Friday 5	Saturday 6
8:45	<b>OPENING</b>			
<b>Chairperson</b>	<b>Spyros Perlepes</b>	<b>Catherine Raptopoulou</b>	<b>K. Papatriantafyllopoulou</b>	<b>Anastasios Tasiopoulos</b>
9:00-9:15	Karl Wieghardt	Albert Escuer	Susan Oliver	Mohamed Eddaoudi
9:15-9:30				
9:30-9:45	Piotr Kaszynski	Małgorzata Holyńska	Sophia Hayes	Stefania Grecea
9:45-10:00				
10:00-10:15	Sokrates Pantelides	Adeline Fournet	Zoi Lada	Manolis Manos
10:15-10:30		Alexandros Perivolaris	Svetlana Eliseeva	
10:30-10:45	Chrysostomos Chatgililoglu	Konstantina Papatriantafyllopoulou	Annaliese Thuijs	Antigoni Margariti
10:45-11:00		Christrina Polyzou	Maria Chrysina	Georgios D. Tarlas
11:00-11:30	<b>Coffee break</b>	<b>Coffee break</b>	<b>Coffee break</b>	<b>Coffee break</b>
<b>Chairperson</b>	<b>Sokrates Pantelides</b>	<b>Giannis Papaefstathiou</b>	<b>Costas Milios</b>	<b>M. Karakassides</b>
11:30-11:45	Gabriel Aeppli	Shengqian Ma	Lawrence Gahan	Rodolphe Clerac
11:45-12:00				
12:00-12:15	Hae-Jin Kim	Theodoros Lazarides	Maria Louloudi	Kathryn Preuss
12:15-12:30				
12:30-12:45	John Papanikolas	John C. Plakatouras	Patrina Paraskevopoulou	Theocharis Stamatatos
12:45-13:00				
13:00-13:15	Stefan Jurga	Andreas Kourtellaris	Ming-Hsi Chiang	T. David Harris
13:15-13:30		Dinos Efthymiou		
13:30-13:45		Kim Christou	Andrew Mowson	Angelos B. Canaj
13:45-14:00	<b>Lunch</b>		<b>Lunch</b>	<b>Lunch</b>
14:00-16:00		<b>Lunch</b>		
<b>Chairperson</b>	<b>Stefan Jurga</b>	<b>Nikos Ioannidis</b>	<b>George Christou</b>	<b>Yiannis Sanakis</b>
16:00-16:15	Rudolf J. Wehmschulte	Colette Boskovic	Allan Blackman	Stephane Petoud
16:15-16:30				
16:30-16:45	Saeed Al Hassan	Curtis Berlinguette	Jeffrey Zaleski	John McGrady
16:45-17:00				
17:00-17:15	Marios Katsiotis	Greta Patzke	Malcolm Halcrow	Dimitrios Gournis
17:15-17:30				
17:30-18:00	<b>Coffee break</b>	<b>Coffee break</b>	<b>Coffee break</b>	<b>Coffee break</b>
<b>Chairperson</b>	<b>George Mitrikas</b>	<b>Vassilis Psycharis</b>	<b>Hae-Jin Kim</b>	<b>Georgios Papavassiliou</b>
18:00-18:15	Corine Mathoniere	Horst Borrmann	Michael Karakassides	George Mitrikas
18:15-18:30				
18:30-18:45	Panayotis Kyritsis	Michael Pissas	Yasser Al Wahedi	Michael Fardis
18:45-19:00				
19:00-19:15	Danna Freedman	Yeong-Ah Soh	Yiannis Deligiannakis	<b>CLOSING</b>
19:15-19:30				
19:30-19:45	Katerina Lazarou	Angelos Mavromatidis	Eleni Efthimiadou	
19:45-20:00			Karine Heuze	
		<b>DINNER</b>		



## TIMETABLE

Wednesday June 3, 2015

**8:45 Official Opening**

**Chairperson: Spyros Perlepes**

**09:00 Karl Wieghardt**

Coordination Chemistry with Organic  $\pi$ -Radicals: Where are the Electrons?

**09:30 Piotr Kaszynski**

Liquid Crystalline Derivatives of  $\pi$ -delocalized Radicals

**10:00 Sokrates Pantelides**

A Discovery of a Novel Form of Crystalline Order Suitable for Thermoelectric Applications

**10:30 Chrysostomos Chatgililoglu**

Biomimetic Models of Radical Stress and Related Biomarkers

**11:00 *Coffee break***

**Chairperson: Sokrates Pantelides**

**11:30 Gabriel Aeppli**

Electron Spin-based Biosensing

**12:00 Hae-Jin Kim**

Electronic and Magnetic Properties of Mn Doped ZnO Nanocrystal

**12:30 John Papanikolas**

Visualization of Charge Carrier Dynamics in Nanowires with Pump-Probe Microscopy

**13:00 Stefan Jurga**

Nanocomposite Copolymer Films Characterized by Long-range Domain Order

**13:30 *Lunch break***

**Chairperson: Stefan Jurga**

**16:00 Rudolf J. Wehmschulte**

Cationic Group 13 Compounds: Very Strong Lewis Acids and Some Surprisingly Weak Ones

**16:30 Saeed Al Hassan**

Sulfur-based Materials

**17:00 Marios Katsiotis**

The Role of Aluminum Coordination & Water Mobility in Y Nanozeolites: A High Temperature NMR Study

**17:30 *Coffee Break***

**Chairperson: George Mitrikas**

**18:00 Corine Mathoniere**

Looking for Photomagnetic Single Molecule Magnets

**18:30 Panayotis Kyritsis**

Magnetostructural Correlations in M(II), M = Fe, Co, Ni and Mn(III) Complexes Bearing the  $[R_2P(E)NP(E)R_2]^-$  Chelating Ligands, E = O, S, Se; R = Ph, <sup>i</sup>Pr

**19:00 Danna Freedman**

Rational Synthetic Approaches to the Design of Qubits

**19:30 Katerina Lazarou**

Seven Coordinate Pentagonal Bipyramidal Mononuclear Mn(II) Complexes

**19:45 *Closing***



**Thursday 4, 2015**

**Chairperson: Catherine Raptopoulou**

**09:00 Albert Escuer**

Azido in Cluster Chemistry: Ancient Times, Current Status and Perspectives

**09:30 Malgorzata Holyńska**

New Oxime Ligands in the Chemistry of Polynuclear Metal Complexes

**10:00 Adeline Fournet**

The Effect of Subtle Environmental Influences on the Magnetic Properties of a Mn<sub>12</sub> Single-Molecule Magnet

**10:15 Alexandros Perivolaris**

Metal-Assisted Ligand Transformations, Chemical Reactivity and Magnetism in Nickel Oximate Clusters

**10:30 Konstantina Papatriantafyllopoulou**

New Structural Types from the Use of Polyol Type Ligands in Mn, Mn/Ni and Mn/Ln Cluster Chemistry

**10:45 Christrina Polyzou**

Nickel(II) /Lanthanide(III) Complexes: Synthetic, Structural and Magnetic Studies

**11:00 *Coffee break***

**Chairperson: Giannis Papaefstathiou**

**11:30 Shengqian Ma**

Nanospace within Metal-Organic Frameworks: Plenty of Opportunities for Heterogeneous Catalysis

**12:00 Theodoros Lazarides**

Synthesis and Photophysical Properties of New Lanthanide Metal-Organic Frameworks

**12:30 John C. Plakatouras**

Flexibility of Ligands as a Source of Structural Pluralism in Coordination Polymer Chemistry

**13:00 Andreas Kourtellaris**

A Microporous Cobalt and Iron Metal Organic Framework with Isonicotinic Acid

**13:15 Dinos Efthymiou**

Flexible Lanthanide MOFs as Highly Selective and Reusable Liquid MeOH Sorbents

**13:30 Kim Christou**

**14:00 *Lunch break***

**Chairperson: Nikos Ioannidis**

**16:00 Colette Boskovic**

Mixed-metal, Mixed-valence, Nanoscale Hybrid Polyoxometalates

**16:30 Curtis Berlinguette**

Interfacial Dynamics in the Dye-Sensitized Solar Cell

**17:00 Greta Patzke**

Tuning Strategies for Cluster-Based Water Oxidation and Reduction Catalysts

***17:30 Coffee Break***

**Chairperson: Vasilis Psycharis**

**18:00 Horst Borrmann**

Purity in Crystal Structures

**18:30 Michael Pissas**

Vortex Matter Properties of  $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$  Superconductor Probed by ac Susceptibility Measurements

**19:00 Yeong-Ah Soh**

Geometric Factors in the Magnetoresistance of InAs

**19:30 Angelos Mavromatidis**

A Review of Hydrocarbon Exploration in Western Greece and its Potential

***20:00 Closing***

**DINNER**

**Friday 5, 2015**

**Chairperson: K. Papatriantafyllopoulou**

**09:00 Susan Oliver**

Women in Physical Sciences – What's the Problem?

**9:30 Sophia Hayes**

Direct Observation of Ultrafast Long-range Charge Separation in Polymer: Fullerene Heterojunctions

**10:00 Zoi Lada**

Copper(II) and Copper(II)/Lanthanide(III) Coordination Clusters and Polymers Based on Oxime Ligands and Di-2-pyridyl Ketone- Novel Organic Ligand Transformations

**10:15 Svetlana Eliseeva**

Luminescent  $Zn_{16}Ln$  Metallocrown Complexes

**10:30 Annaliese Thuijs**

Synthesis and Characterization of a Variety of Manganese-Zirconium Clusters

**10:45 Maria Chrysina**

Paramagnetic Biocatalysts: Metalloradical Interactions Involving the Water Oxidizing Complex of Photosystem II

***11:00 Coffee break***

**Chairperson: Costas Milios**

**11:30 Lawrence Gahan**

A Heterodinuclear Fe(III)Zn(II) Complex as a Mimic for Purple Acid Phosphatase with Site Specific Zn(II) Binding

**12:00 Maria Louloudi**

Surface Chemistry on Recycled Carbon Materials: Single-Site Heterogeneous Catalysts and Applications

**12:30 Patrina Paraskevopoulou**

Synthesis and Properties of Polydicyclopentadiene Gels

**13:00 Ming-Hsi Chiang**

A High-Performance Diiron Electrocatalyst for Hydrogen Production

**13:30 Andrew Mowson**

Synthesis and Characterization of a Variety of Manganese-Zirconium Clusters

***13:45 Lunch break***

**Chairperson: George Christou**

**16:00 Allan Blackman**

Jahn-Teller, or not Jahn-Teller?

**16:30 Jeffrey Zaleski**

Thermally and Photochemically Activated Diradicals: From Small Molecule Bioreagents to Nanomedicine Applications for Biopolymers

**17:00 Malcolm Halcrow**

Unexpected, Cooperative Spin-Crossover in Iron(II)/Dipyrazolylpyridine Complexes with Large Jahn-Teller Distortions

***17:30 Coffee Break***

**Chairperson: Hae-Jin Kim**

**18:00 Michael Karakassides**

Magnetic Porous Carbon Nanocomposites as Adsorbents and Catalysts for Environmental Remediation

**18:30 Yasser Al Wahedi**

Nanoscale to Industrial Scale - An interesting Case Study

**19:00 Yiannis Deligiannakis**

Synthesis of NanoHeterostructures by 2-Nozzle Flame Spray Pyrolysis: Using Industrial Scale Technology to Lab-scale Experiments

**19:30 Eleni Efthimiadou**

Quatro Stimuli Microspheres as a Versatile Drug Delivery System: Release Properties, In-vivo and In-vitro Study

**19:45 Karine Heuze**

Dendritic Maleimide Functionalization of Core-shell ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/polymer) Nanoparticles for Efficient Bio-immobilization

***20:00 Closing***

**Saturday 6, 2015**

**Chairperson: Anastasios Tasiopoulos**

**09:00 Mohamed Eddaoudi**

Metal-Organic Frameworks from Design Strategies to Applications

**09:30 Stefania Grecea**

Octacyanometallates–Versatile Building–blocks for Constructing Multifunctional Molecular Materials

**10:00 Manolis Manos**

Alkaline Earth Metal Ion/Dihydroxy-Terephthalate MOFs: Structural Diversity and Unusual Luminescent Properties

**10:30 Antigoni Margariti**

Oxalamide Based Metal-Organic Frameworks

**10:45 Georgios D. Tarlas**

Metal-Organic Frameworks for Sensing Applications

**11:00 *Coffee break***

**Chairperson: Michael Karakassides**

**11:30 Rodolphe Clerac**

Optical and Magnetic Molecular Switches from Solid State to Solutions

**12:00 Kathryn Preuss**

Magnetic Properties of Metal-Radical Complexes using Thiazyl Ligands

**12:30 Theocharis Stamatatos**

Naphthalene-based Diols as Bridging Ligands in Polynuclear Metal Cluster Chemistry: Synthesis, Structures and Magnetic Properties

**13:00 T. David Harris**

Synthesis of Benzoquinonoid Radical-Containing Materials with Strong Magnetic Exchange Coupling

**13:30 Angelos B. Canaj**

Nonanuclear  $[\text{Ni}_6\text{Ln}_3]$  Cages: Trapped  $[\text{Ln}^{\text{III}}_3]$  Triangles inside  $[\text{Ni}^{\text{II}}_6]$  Trigonal Prisms and a  $[\text{Ni}_6\text{Dy}_3]$  Single Molecule Magnet

**13:45 *Lunch break***

**Chairperson: Yiannis Sanakis**

**16:00 Stephane Petoud**

Paramagnetic Nanomaterials for Optical Biological Imaging: MOFs Incorporating Lanthanide Cations Emitting in the Near-Infrared

**16:30 John McGrady**

In Search of Structure-activity Relationships in Paramagnetic Molecular Wires

**17:00 Dimitrios Gournis**

Graphene Pillaring: Towards Novel Multifunctional Materials

**17:30 *Coffee Break***

**Chairperson: Georgios Papavassiliou**

**18:00 George Mitrikas**

ESEEM spectroscopy: Basic theory and application examples

**18:30 Michael Fardis**

NMR Studies of Electronic Properties and Local Densities of States in Bulk and Nanoparticle Transition Metal Phosphides

**DEPARTURE**

## **Electron Spin-based Biosensing**

Gabriel Aeppli

*Paul Scherrer Institute, Switzerland*

*Email: [gabriel.aeppli@psi.ch](mailto:gabriel.aeppli@psi.ch)*

Optical and spin-based microwave assays for protein folding and interactions are reviewed. In particular, we examine electron paramagnetic resonance-based antigen detection using a bridging maleimide with a spin label; the resulting assay works in human blood, and also can be used to examine thermal denaturation.

### References:

Schumacher et al., Scientific Reports 3, Article Number: 1525 doi:10.1038/srep01525 (2013)

Sagar et al, Scientific Reports 3, Article Number: 2130 doi:10.1038/srep02130 (2013)



## **Sulfur-based Materials**

Saeed M. Alhassan

*Department of Chemical Engineering, The Petroleum Institute  
Abu Dhabi, United Arab Emirates*

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Sulfur is an interesting element with unique properties. In its native state, it exists as rings of 8 atoms called cyclo-octasulfur or  $S_8$  for short. Sulfur is produced naturally in volcanos and synthetically as a byproduct of separating of hydrogen sulfide from hydrocarbon in oil and gas industry. It is predicted that sulfur supply in the next few years will outpace demand which lead to a surplus of sulfur with limited applications. In recent years, sulfur is being considered in relatively newer applications due to its abundance and certain unique properties especially in the field of electrochemistry and optics.

In few years, United Arab Emirates will be top producer of the yellow element. With that in mind and the fact that sulfur has limited application, we will present our recent efforts in developing new applications for sulfur. Among the most promising applications are the development of highly-filled polymeric composites of sulfur and polymers and developing inorganic sulfur based foams. We will discuss fabrication of these materials as well as their thermal, mechanical and transport properties.

## Nanoscale to Industrial Scale - An interesting Case Study

Yasser F. Al Wahedi

<sup>a</sup>*Gas Research Center, Abu Dhabi Petroleum Institute, P.O. Box 2533, Abu Dhabi, United Arab Emirates*

*Email: yaalwahedi@pi.ac.ae*

Development of new materials for specific applications from fundamental perspective is commonly perceived as a distinct initial phase during the course of technology development. Process scale up and economic assessment only comes at the next stage. While such an approach grants the unconstrained environment for technology development, it can cause loss of several man-years of spent due to un-competitiveness in the commercial market. Coupling the two phases can reap numerous benefits. Herein we present a case study where we show how process scale up computations and economic assessment can assist material development by setting targeted material properties. The case study pertains to the Claus Tail Gas Treatment process.

Current cost figures suggests that enhancing the recovery of a Claus unit to achieve the target set by environmental regulations (>99.9%) from its current limit of 98% can lead to the doubling in the Capital and operating costs [1]. Clearly, there is a business need towards achieving the set target at the lowest possible cost. The presented case study investigates the efficacy of a swing based adsorption system in achieving the set target. By looking at the cost of scaled system given a conventional adsorbent, we identify the crucial adsorbent properties to be targeted during the adsorbent development stage. Furthermore, the initial cost figures suggest that the concept of adsorption swing holds promising potential in meeting the business need. Such an early indication on the economic competitiveness of the proposed technology is vital.

[1] Strickland, J.F., Quinlan M., Velasquez D., Lepin D., Meyer H., *Tail Gas Clean-Up Processes: Capabilities and Relative Costs*, **2000**.

## Interfacial Dynamics in the Dye-Sensitized Solar Cell

Berlinguette, C. P.\*

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2036 Main Mall, Vancouver, B.C. Canada*

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Our program has developed a series of cyclometalated ruthenium(II) complexes of type  $[\text{Ru}^{\text{II}}(\text{N}^{\wedge}\text{N})_2(\text{C}^{\wedge}\text{N})]^{\text{Z}}$  to accomplish the requisite light-absorption and charge-separation events in the dye-sensitized solar cell (DSSC). This class of molecules offers a distinct advantage over conventional ruthenium-based dyestuff for DSSC applications because the replacement of the  $\text{NCS}^-$  ligands with aromatic ligands presents the opportunity to manipulate both the ground- and excited-state energy levels. This presentation will detail how the careful design of this class of compounds has yielded unprecedented resolution of key reaction steps in the DSSC, including regeneration of oxidized dyes, and intra- and inter-molecular hole-transfer at the semiconductor interface.

## Jahn-Teller, or not Jahn-Teller?

A. G. Blackman<sup>a,\*</sup>, N. A. Hall<sup>b</sup>, A. Deronzier<sup>b</sup>, C. Duboc<sup>b</sup> and M-N. Collomb<sup>b</sup>

*a) School of Applied Sciences, Auckland University of Technology, Auckland, New Zealand*

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The Jahn-Teller effect is usually manifested as an elongation of two *trans* metal-ligand bonds in 6-coordinate complexes having partially occupied  $e_g$  orbitals, and the classic examples are generally found in complexes of  $\text{Cu}^{2+}$ . Much rarer are systems in which the degeneracy of the  $e_g$  orbitals is broken by a compression of two *trans* metal-ligand bonds – indeed, such complexes are ‘almost unheard of’ [1]. In this talk, we will present results aimed at determining whether the shortening of two *trans* metal-ligand bonds in the  $[\text{Cu}(\text{bmet})]^{2+}$  complex cation is the result of a genuine Jahn-Teller compression, or simply due to geometric constraints imposed by the bmet ligand.



**Figure 1.** The structures of the bmet ligand (left) and the  $[\text{Cu}(\text{bmet})]^{2+}$  cation (right).

[1] M. A. Halcrow, *Chem. Soc. Rev.*, **2013**,42, 1784.

## Purity in Crystal Structures

H. Borrmann

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*Email: Horst.Borrmann@cpfs.mpg.de*

In natural sciences purity of a certain compound or material is usually defined in terms of chemical composition or based on a physical property. Deviations from the ideal crystal structure are normally not discussed in terms of purity. However, there is good reason to expect that distinct modification of a given structural motif may have a decisive impact on particular properties just like in the well known case of doping in semiconductors.

Recently we observed several cases where a well known crystal structure obviously contains around one to two percent of another well established structural motif. Details will be presented for  $\text{TmAlB}_4$ ,  $\text{CeIrIn}_5$  and  $\text{CeCoIn}_5$ , as well as for  $\text{PtAl}_2$  and  $\text{RuAl}_2$ . Particular magnetic properties in  $\text{TmAlB}_4$  seem to be directly linked to peculiar features in the real structure [1]. Along this line prototypical heavy fermion superconductors  $\text{CeIrIn}_5$  and  $\text{CeCoIn}_5$  were studied in detail [2]. Most remarkable, in all cases no significant deviation from ideal chemical composition was detected.

[1] T. Mori, H. Borrmann, S. Okada, K. Kudou, A. Leithe-Jasper, U. Burkhardt, Yu. Grin, *Phys. Rev. B*, **2007**, 76, 064404.

[2] St. Wirth, Yu. Prots, M. Wedel, St. Ernst, St. Kirchner, Z. Fisk, J.D. Thompson, F. Steglich, Yu. Grin, *J. Phys. Soc. Jpn.*, **2014**, 83, 061009.

## Mixed-metal, Mixed-valence, Nanoscale Hybrid Polyoxometalates

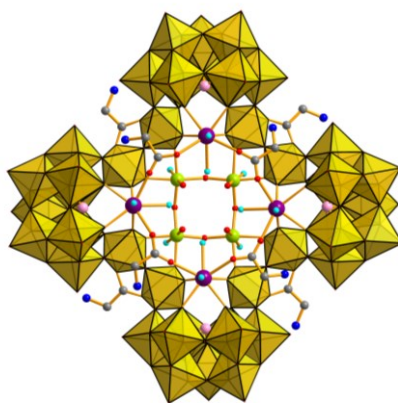
C. Boskovic,\* C. Ritchie, F. Akhlaghi, M. Vonci

*School of Chemistry, University of Melbourne, Vic, 3010, Australia*

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Polyoxometalates (POMs) are molecular analogues of early transition metal oxides, formed from acid condensation of simple oxoanions. They are comprised of linked metal-centered  $\text{MO}_n$  polyhedra, often incorporating additional heteroatoms within the coordination cluster. The reversible and multi-electron redox chemistry that POMs can display confers an ability to access multiple electronic states through chemical, electrochemical or photophysical processes, which has given rise to long-standing applications in analytical chemistry and catalysis.

Functionalisation of a robust POM backbone has afforded a fascinating family of hybrid nanoscale compounds that also incorporate rare earth ions and amino acid ligands (Figure 1). The functionality of the individual analogues arises from the combination of the chemical properties of the constituent components. Site-selective metal substitution, photoreduction and solution stability have been elucidated through a concerted spectroscopic, diffractometric, magnetochemical, electrochemical and theoretical investigation. These features, together with chirality and directable solid state packing, reveal the amenability of this family to multiple compositional modifications that emphasizes their potential as nanoscale molecular materials with tunable properties.[1]



**Figure 1.** Structural representation of hybrid POM  $[\text{As}_4(\text{M}_4)\text{W}_{44}\text{Y}_4\text{O}_{160}(\text{Gly})_8(\text{H}_2\text{O})_{12}]^{8-}$  ( $\text{M} = \text{Mo}, \text{W}$ ).

[1] M. Vonci, F. Akhlaghi Bagherjeri, P. D. Hall, R. W. Gable, A. Zavras, R. A. J. O'Hair, Y. Liu, J. Zhang, M. Field, M. Taylor, J. Du Plessis, G. Bryant, M. Riley, L. Sorace, P. Aparicio, X. López, J. M. Poblet, C. Ritchie, C. Boskovic, "Modular Molecules: Site-Selective Metal Substitution, Photoreduction and Chirality in Polyoxometalate Hybrids", *Chem. Eur. J.* **2014**, *20*, 14102.

# Nonanuclear $[\text{Ni}_6\text{Ln}_3]$ Cages: Trapped $[\text{Ln}^{\text{III}}_3]$ Triangles inside $[\text{Ni}^{\text{II}}_6]$ Trigonal Prisms and a $[\text{Ni}_6\text{Dy}_3]$ Single Molecule Magnet

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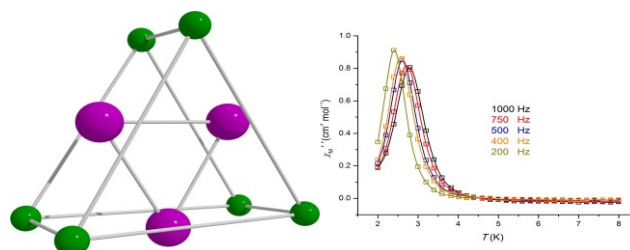
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One of the most active areas in the field of molecular magnetism is the search for molecules that can retain their magnetization in the absence of external magnetic field, and thus function as nanomolecular magnetic species. The number of such species, that are termed as Single Molecule Magnets, SMMs, has grown exponentially over the last two decades and the phenomenon, firstly observed for “traditional” transition metal centres as Mn, Fe, Co, and Ni, now has been expanded to examples including 3d-4d/5d, 3d-4f, 4f- and 5f- molecules. Herein, we present the syntheses, structure and magnetic properties of three new nonanuclear  $[\text{Ni}^{\text{II}}_6\text{Ln}^{\text{III}}_3]$  (Ln= Gd, Dy, Er) cages. AC magnetic susceptibility measurements under zero external field show temperature and frequency dependent out-of-phase peaks for the  $[\text{Ni}^{\text{II}}_6\text{Dy}^{\text{III}}_3]$  analogue, which displays SMM behaviour with  $U_{\text{eff}} = 24$  K (Figure).



**Figure.**(Left) The metallic core of the  $[\text{Ni}^{\text{II}}_6\text{Ln}^{\text{III}}_3]$  cages and (Right) the plot of the out-of-phase  $\chi''_M$  signal vs. temperature for the  $[\text{Ni}^{\text{II}}_6\text{Dy}^{\text{III}}_3]$  analogue.

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## Biomimetic Models of Radical Stress and Related Biomarkers

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The biological consequences of free radical production are the central subject of a very lively scientific debate, focusing on the estimation of the type and extent of damage, as well as the efficiency of the protective and repair systems. When studying free radical based chemical mechanisms, it is very important to establish biomimetic models, which allow the experiments to be performed in a simplified environment, but suitably designed to be in strict connection with cellular conditions. The biomimetic modeling approach has been coupled with physical organic chemistry methodologies and knowledge of free radical reactivity. Molecular basis of important processes have been identified, building up molecular libraries of products concerning unsaturated lipids, sulfur-containing proteins and nucleic acids, to be developed as biomarkers. Ongoing projects in our group deal with lipidomics,<sup>1,2</sup> genomics<sup>3</sup> and proteomics<sup>1</sup> of free radical stress and some examples will be described.

For recent reviews, see:

- [1] Chatgililoglu, C.; Ferreri, C.; Melchiorre, M.; Sansone, A.; Torreggiani, A. *Chem. Rev.* **2014**, *114*, 255.
- [2] Ferreri, C.; Chatgililoglu, C. *Expert Rev. Mol. Diagn.* **2012**, *12*, 767.
- [3] Chatgililoglu, C.; Ferreri, C.; Terzidis, M. A. *Chem. Soc. Rev.* **2011**, *40*, 1368.

# A High-Performance Diiron Electrocatalyst for Hydrogen Production

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A diiron dithiolate complex bears an analog to the two-electron reduced species of  $[(\mu\text{-bdt})\text{Fe}_2(\text{CO})_6]$  is synthesized. First protonation occurs onto the Fe–Fe vector to form the Fe bridging hydride species. Subsequent protonation onto the thiolate site occurs in the presence of additional acids. This step is to yield the most thermodynamically favored species according to the results of the DFT calculation. The first di-protonated  $[\text{FeFe}]$  hydrogenase model compound containing the S-proton is also successfully isolated and characterized. The results provide insights to elucidate the role of the Fe and S sites in coordination within the molecular catalyst at the reduced state in a pool of free protons. It is suggested that the thiolate sulfur acts a determining site for accepting protons during the catalytic processes. Under acidic condition, this diiron electrocatalyst conducts the production of hydrogen at a potential of  $-1.17\text{ V}$  (versus the ferrocenium/ferrocene couple). The turnover frequency over  $2 \times 10^5\text{ s}^{-1}$  is estimated for the catalysis of weak acid. The higher turnover frequency and current density are achieved in the presence of acids with medium strength. The experimental and DFT calculation results suggest that an energetic transient species is generated via the concerted proton-electron transfer pathway for fast catalysis.

## Paramagnetic Biocatalysts: Metalloradical Interactions Involving the Water Oxidizing Complex of Photosystem II

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Photosystem II is a membrane multi - subunit protein complex which catalyzes the photoinduced water oxidation in plants, algae and cyanobacteria. Absorption of a photon by antennae chlorophylls eventually leads to the oxidation of a special cluster of chlorophylls, termed  $P_{680}$ ; the electron is transferred to acceptor side iron-quinone complex,  $Q_AFe^{2+}Q_B$ . The positive charge on  $P_{680}$  is neutralized by an electron transfer from a  $Mn_4CaO_5$  cluster, which binds the substrate  $H_2O$  molecules. Following absorption of four photons, four electrons are transferred from the  $Mn_4CaO_5$  cluster to two quinone  $Q_B$  molecules, four  $H^+$  are released to the bulk, and one molecule of  $O_2$  is formed. Therefore, the catalytic cycle of the  $Mn_4CaO_5$  cluster undergoes four transitions, called S – transitions:  $S_0 \rightarrow S_1$ ,  $S_1 \rightarrow S_2$ ,  $S_2 \rightarrow S_3$ ,  $S_3 \rightarrow (S_4) \rightarrow S_0$ . Tyrosine ( $Tyr_Z$ ), an aminoacid residue near  $Mn_4CaO_5$ , acts as an intermediate electron carrier between the cluster and  $P_{680}$ , and in parallel it influences  $H^+$  removal. Low-temperature EPR spectroscopy was employed in order to trap and study intermediates, including the free radical  $Tyr_Z^{\cdot}$  interacting with the  $Mn_4CaO_5$ , during the two critical transitions  $S_2 \rightarrow S_3$  and  $S_3 \rightarrow S_0$ .

## Optical and Magnetic Molecular Switches from Solid State to Solutions

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The design of molecule-based systems displaying tunable optical and/or magnetic properties under external stimuli received a great deal of attention in the past few years. This interest is driven by the potential applications in high-performance molecule-based electronics. As an example, 3D Fe/Co Prussian blue compounds exhibit a concomitant change in magnetic and optical properties due to a temperature- or light-induced metal-to-metal electron transfer (ET). The foregoing remarkable properties in Prussian blues prompted us to design soluble molecular fragments of these coordination networks through a rational building-block approach in order to mimic their properties on a single molecule.<sup>[1-4]</sup> With a judicious choice of the ligands for metal ion precursors, we prepared a octanuclear,<sup>[1]</sup> tetranuclear<sup>[2]</sup> and recently dinuclear<sup>[3]</sup> cyanido-bridged Fe/Co complexes. In the solid state, while an intramolecular ET is observed for the [Co<sub>4</sub>Fe<sub>4</sub>] and [Co<sub>2</sub>Fe<sub>2</sub>] complexes,<sup>[1,2]</sup> the Co ion of our first dinuclear complex exhibits a spin crossover (SCO) involving a [Fe<sup>III</sup><sub>LS</sub>-CN-Co<sup>II</sup><sub>LS</sub>] ground state and a thermally populated [Fe<sup>III</sup><sub>LS</sub>-CN-Co<sup>II</sup><sub>HS</sub>] state.<sup>[3]</sup> To our knowledge, this compound is the only example of a heterobimetallic complex exhibiting a Co<sup>II</sup> SCO. Remarkably, our studies of these [Co<sub>n</sub>Fe<sub>n</sub>] complexes in solution reveal important optical and magnetic changes induced by an intramolecular metal-to-metal ET triggered and modulated by a controlled protonation of the complex, by the solvent nature or by temperature. Therefore, these molecules act as different molecular switches depending on their physical state and external stimuli.<sup>[3]</sup> These results motivated us to design new dinuclear [FeCo] complexes exhibiting both thermally and light induced electron transfer in solid state. Learning from these previous systems, new dinuclear complexes<sup>[4]</sup> have been designed by a rational building-block approach. Combined structural, spectroscopic, magnetic and photomagnetic studies reveal that a metal-to-metal electron transfer that can be triggered by light, temperature and lattice contents is observed for the first time in solid state for a dinuclear cyanido-bridged Fe/Co complex.<sup>[4]</sup>

[1]. D. Li et al., *J. Am. Chem. Soc.* 130, 252-258 (2008).[2]. Y. Zhang et al., *Angew. Chem. Int. Ed.* 49, 3752-3756 (2010) ; D. Siretanu, et al., *Chem. Eur. J.* 17, 11704-11708 (2011) ; Y. Zhang et al., *J. Am. Chem. Soc.* 136, 16854-16864 (2014).[3]. I.-R. Jeon, et al., *Chem. Sci.* 4, 2463-2470 (2013).[4]. E. S. Koumoussi et al., *J. Am. Chem. Soc.* 136, 15461-15464 (2014).

# Synthesis of NanoHeterostructures by 2-Nozzle Flame Spray Pyrolysis: Using Industrial Scale Technology to Lab-scale Experiments

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Flame Spray Pyrolysis is an one-step technology for production of nanoparticles with size varying in the range of few nm to 100nm [1,2]. FSP allows production of solvent-free nanopowders of almost all metal-oxides (superparamagnetic, semiconducting, ferroelectric, catalytic, ceramic, optical etc) as well as metallic nanoparticles from noble metals. (Ag, Au, Pt, Pd etc) [3]. Currently FSP is used by Degussa/Evonik, Johnson Matthey, Cabot for large scale production of TiO<sub>2</sub>, ZnO for commercial use. Herein we discuss a 2-Nozzle FSP system for the production of Nano-Heterostructures consisting of two types of nanoparticles tightly associated via neck-sintering. This provides novel physical systems with unprecedented properties.

We will detail a novel [TiO<sub>2</sub>@Ag<sup>0</sup>] system which is a “black titania” material that is produced via Strong Metal-Support Interaction (SMSI) in the FSP system. The photophysical properties of the black-TiO<sub>2</sub>@Ag<sup>0</sup> studied by Electron Paramagnetic Resonance (EPR) spectroscopy, reveal a novel suboxide phase Ti<sub>4</sub>O<sub>7</sub> that is rich in surface-electrons.

[1] Pratsinis, S. E. "Flame aerosol synthesis of ceramic powders". *Progress in Energy and Combustion Science* **1998**, 24, 197–219.

[2] Strobel, R.; Pratsinis, S. E. "Flame aerosol synthesis of smart nanostructured materials". *Journal of Materials Chemistry* **2007**, 17, 4743–4756.

[3] W.Y. Teoh, et al. "Flame spray pyrolysis: An enabling technology for nanoparticles design and fabrication". *Nanoscale*, **2010**, 2, 1324–1347.

[4] Fujiwara, K., Deligiannakis, Y., Skoutelis, C.G., Pratsinis, S.E. Visible-light active black TiO<sub>2</sub>-Ag/TiO<sub>x</sub> particles, *Applied Catalysis B: Environmental* **2014**, 154-155, 9-15.

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# **Metal-Organic Frameworks from Design Strategies to Applications**

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Demand for functional materials targeted for specific applications is ever increasing as societal needs and demands mount with advancing technology. One class of inorganic-organic hybrid materials, metal-organic frameworks (MOFs), has burgeoned in recent years due, in part, to effective design strategies (i.e. reticular chemistry) for their synthesis and their inherent [and readily interchangeable] hybrid, highly functional character. Metal-organic materials, specifically metal-organic frameworks (MOFs), have emerged as a unique class of materials amenable to design and manipulation for desired function and application. Several design strategies have been utilized and developed to target viable MOF platforms, from the single-metal-ion molecular building block (MBB) approach to the hierarchical supermolecular building block and supermolecular building layer approaches (SBB and SBL, respectively). This inherent built-in information allows access to highly stable and made-to-order porous materials toward applications pertaining to energy and environmental sustainability. Specifically, materials for CO<sub>2</sub> separation and capture will be highlighted, as well as insights into MOF membrane construction and respective gas separation properties.

## Luminescent Zn<sub>16</sub>Ln Metallacrown Complexes

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A number of modern advanced technologies rely on the unique spectroscopic properties of lanthanide(III) ions. In particular, their ability to generate characteristic sharp emission bands in the near-infrared (NIR) ranges has a growing interest in view of the exponentially growing number of applications in bioanalysis and optical imaging.[1] The main fundamental challenges for the design of NIR-emitting lanthanide(III) compounds are: (i) an efficient sensitization through appropriate chromophores, and (ii) an efficient protection from non-radiative deactivations through O-H, N-H and C-H vibrations.

We have recently demonstrated that Zn<sub>16</sub>Ln “encapsulated sandwich” metallacrowns (MC) obtained by the self-assembly of Ln(III), Zn(II) ions and tetradentate chromophoric ligands, quinaldichydroxamic acid (quinHA), is an innovative and versatile approach allowing the precise localization of lanthanide ions at a predetermined and shielded position to achieve high quantum yields and long luminescence lifetimes.[2] In addition, such MCs possess very good photostability.

Here, we expand this strategy to Zn<sub>16</sub>Ln MCs assembled from derivatives of pyrazinehydroxamic acid with the goal to improve biocompatibility and further shift excitation wavelength towards the visible/NIR range.

[1] Bünzli J.-C.G. *Chem. Rev.* **2010**, *110*, 2729-2755.

[2] Trivedi, E.R.; Eliseeva S.V.; Jankolovits J.; Olmstead M.M.; Petoud S.; Pecoraro V.L., *J. Am. Chem. Soc.* **2014**, *136*, 1526-1534.



## **Quatro Stimuli Microspheres as a Versatile Drug Delivery System: Release Properties, In-vivo and In-vitro Study**

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A versatile drug carrier in microsphere shape that responds to external stimuli is synthesized *via* the emulsion polymerization process. This facile two-step process is carried out by using Poly (Methyl Methacrylate) as a soft sacrificed template and a series of monomers with desired properties as coating materials. The highlight of this work is the formation of inner cavity that is created inside the microspheres during the shell fabrication (2nd step). The surface of the multi-stimuli microcontainers is functionalized with magnetite nanoparticles in order to attach sensitivity in external alternating magnetic field (AMF). By using AMF in various strengths and frequencies, the temperature of the final multi-stimuli microcontainers (Q-Spheres) increases in a control manner resulting in hyperthermia phenomenon. Loading and release studies are carried out using the anthracycline drug Doxorubicin in different stimuli and the cytotoxicity is evaluated by using the MTT assay. *In vivo* studies were performed after-Q-spheres radiolabelling with <sup>99m</sup>Tc which intravenously injected on female normal Swiss mice and their biodistribution study was also carried out.

# Flexible Lanthanide MOFs as Highly Selective and Reusable Liquid MeOH Sorbents

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The post-synthesis modification of MOFs is based on their chemical transformation after they have been synthesized and is preferable to proceed in a single-crystal-to-single crystal (SCSC) fashion in order to gain direct structural information for the modified compounds via their characterization with single crystal X-ray crystallography. Our group has been investigating the synthesis of new Lanthanide metal-organic frameworks (LnMOFs) and studies their SCSC coordinating solvent exchange properties. The first result of these studies included the isolation of a flexible Nd<sup>3+</sup>MOF [Nd<sub>2</sub>(CIP)<sub>2</sub>(DMF)<sub>2.8</sub>(H<sub>2</sub>O)<sub>1.2</sub>] (**UCY-2**), based on the semi-rigid tricarboxylic ligand H<sub>3</sub>CIP, which showed an extraordinary capability to undergo a series of SCSC transformations. [1] This study represents the initial demonstration of the SCCSE as a powerful method for the controlled modification of the structures of Ln-MOFs.

A series of new Lanthanide metal-organic frameworks (LnMOFs), structurally related to **UCY-2** will be presented. Their structural, spectroscopic and magnetic studies will be discussed. Emphasis will be given in the ability of the flexible LnMOF [Ce<sub>2</sub>(CIP)<sub>2</sub>(DMF)<sub>4</sub>] (**UCY-5**) to behave as highly efficient sorbent for MeOH in the liquid phase due to its capability to absorb MeOH not only as guest but also as ligand for the lanthanide ion. The results of the sorption experiments indicate an exceptional capability to absorb liquid MeOH and fast kinetics, while the sorbent is reusable and is also capable of highly selective sorption of MeOH over EtOH. [2].

[1] E. J. Kyprianidou, M. J. Manos, G. S. Papaefstathiou, A. J. Tasiopoulos, *Inorg. Chem.*, **2012**, 51, 6308

[2] C. G. Efthymiou, E. J. Kyprianidou, C. J. Milios, M. J. Manos, A. J. Tasiopoulos, *J. Mater. Chem.*, **2013**, 1, 5061

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# Azido in Cluster Chemistry: Ancient Times, Current Status and Perspectives

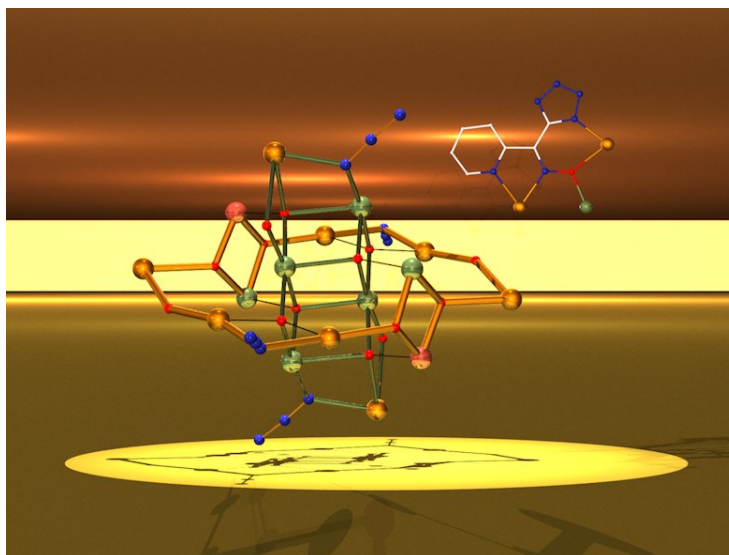
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The azido anion has been widely employed as a bridging ligand during the last decades, allowing the characterization of a great variety of 1D, 2D or 3D extended networks and a large number of molecular systems with nuclearities ranging from  $M_2$  to impressive  $M_{32}$  giant clusters. [1] Coordination modes and their behavior as superexchange pathway is well established and the ferromagnetic response of its  $\mu_{1,1}$  (end-on) coordination mode has been systematically employed to get high spin clusters, which often exhibit SMM response.

The aim of this presentation is to give an overview of the history of this ligand, from the early  $Cu_2$  systems studied during the 70's until today, paying special attention to the more relevant research groups related with the azido ligand and their contribution to develop interesting magnetic systems.



[1] Escuer, A.; Esteban, J.; Perlepes, S. P.; Stamatatos, T. C., *Coordination Chemistry Review*, **2014**, 275, 87-129.

# NMR Studies of Electronic Properties and Local Densities of States in Bulk and Nanoparticle Transition Metal Phosphides

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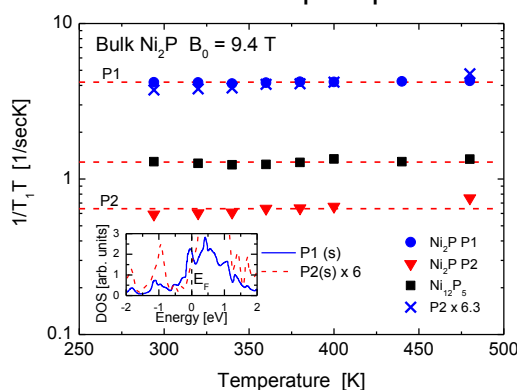
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Catalytic processes are at the core of any petroleum refinery worldwide, including cracking reactions, alkylation, and sulphur removal. Nanosized catalysts have been recently introduced in an effort to improve catalytic properties. Transition metal phosphides are currently of great interest because they exhibit catalytic activity such as hydro-desulphurization and hydro-denitrogenation in petroleum industry.

Nuclear magnetic resonance (NMR) is a suitable microscopic tool to investigate the electronic structure of metallic materials based on the conduction electron-nuclear spins interactions. The  $T_1$  spin-lattice relaxation rates, for example, are proportional to the square of appropriate components of the electron density of states (DOS) at the Fermi level. Besides, the resonance (Knight) shift is related to the electronic environment of the resonating nucleus.

In this work, the local density of states at the phosphorous site in bulk and nanoparticle nickel phosphides  $\text{Ni}_2\text{P}$  has been examined using  $^{31}\text{P}$  NMR. The NMR spectra and the  $1/T_1$  rates have been measured as functions of temperature. From the NMR spectra two P lines with very different NMR shifts have been detected corresponding to the two P in the unit cell. The relaxation rates follow a linear law characteristic of hyperfine interactions with conduction electrons revealing the metallic behaviour of the materials. The correlation between the NMR response and the electronic structure of these transition metal phosphides is discussed.



**Figure.** Temperature dependence of the experimental  $1/T_1T$  in bulk  $\text{Ni}_2\text{P}$  showing the different values of the relaxation rates at the two NMR peaks (P1 and P2) in  $\text{Ni}_2\text{P}$  as well as a contribution of a minor phase  $\text{Ni}_{12}\text{P}_5$ . The dashed lines represent the weighted averages of  $1/T_1T$ . The inset shows the P(s) contribution of the total computed DOS around  $E_F$  in  $\text{Ni}_2\text{P}$  for the two independent P1 and P2 atoms (from Bekaert et al., J. Phys. Chem. C **2008**, 112, 20481-20490).

# **The Effect of Subtle Environmental Influences on the Magnetic Properties of a Mn<sub>12</sub> Single-Molecule Magnet**

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The well-studied family of single-molecule magnets, [Mn<sub>12</sub>O<sub>12</sub>(O<sub>2</sub>CR)<sub>16</sub>(H<sub>2</sub>O)<sub>4</sub>], has a very characteristic magnetic signature arising from the strongly ferromagnetic Mn<sup>IV</sup>...Mn<sup>IV</sup> and antiferromagnetic Mn<sup>III</sup>...Mn<sup>IV</sup> interactions in the core, and very little to no intermolecular interactions. The  $S = 10$  ground state resulting from these interactions has been observed in all Mn<sub>12</sub> derivatives studied to date, and usually results in a  $\chi_m T$  maximum at 50 - 55 cm<sup>3</sup> K mol<sup>-1</sup> at low temperature. In the present work, we are studying the effect on the magnetic properties of modifications to the local environment of one of these Mn<sub>12</sub> single-molecule magnets, that with R = C<sub>6</sub>H<sub>4</sub>-p-F. It has been observed that even minor perturbations can cause significant changes to the magnetic data, while still retaining the SMM behavior. In an attempt to gain an understanding of the correlation between the local environment of the molecules and their magnetic properties, several systematic modifications to their environment have been made, and their effect observed, as well as their reversibility. The results of this study will be presented.

## **Rational Synthetic Approaches to the Design of Qubits**

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Quantum computation has the potential enable the accurate simulation of quantum systems, model complex needle-in-a-haystack type problems such as protein folding and break codes. Yet, solving this challenge is decades away; current research focuses on the smallest unit of a quantum computer, a qubit. Any object that can be placed into a superposition of two states such as a proton spin or an electronic spin can be employed as a qubit. Magnetic molecules offer great promise for quantum computation due to their facile tunability and reproducible behavior. Yet, magnetic species have the disadvantage of short operating times due to rapid electronic spin decoherence. Using rational synthetic design, we are developing fundamental insight into the underlying principles that govern decoherence and creating a set of design parameters for the synthesis of viable electronic-spin qubits.

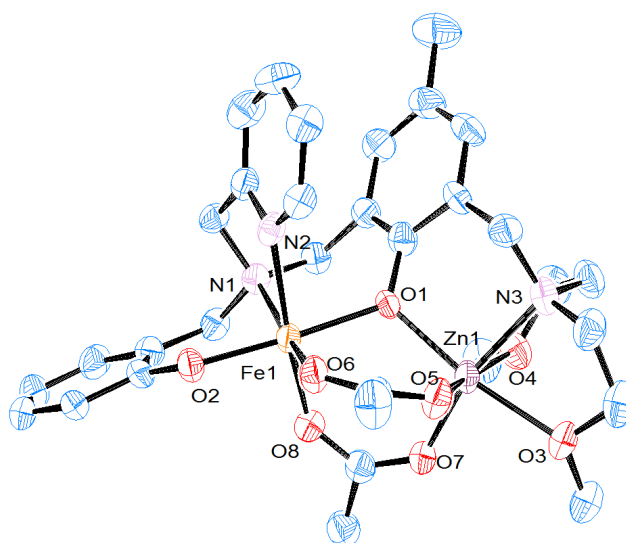
# A Heterodinuclear Fe(III)Zn(II) Complex as a Mimic for Purple Acid Phosphatase with Site Specific Zn(II) Binding

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Purple acid phosphatases (PAPs) are the only binuclear metallohydrolases where the necessity for a heterovalent active site (Fe(III)-M(II), M = Fe, Zn or Mn) for catalysis has been established. A major goal for the synthesis of PAP biomimetics is to design a ligand in which the two coordination sites exhibit discrimination between the trivalent and divalent metal ions. With this goal in mind the ligand 2-((bis(2-methoxyethyl)amino)methyl)-6-(((2-hydroxybenzyl)(2-pyridylmethyl)amino)methyl)-4-methylphenol (BMMHPH<sub>2</sub>), with two distinct coordination sites, N<sub>2</sub>O<sub>2</sub> ( $\alpha$ ) and NO<sub>3</sub> ( $\beta$ ), has been prepared. Although not exactly mimicking the active site of PAP, the ligand facilitated the formation of the complex [FeZn(BMMHP)(CH<sub>3</sub>COO)<sub>2</sub>](BPh<sub>4</sub>) which exhibited regioselectivity in the two metal binding sites. The phosphoesterase-like activity of the complex in 50:50 acetonitrile/water was investigated using the substrate bis(2,4-dinitrophenyl) phosphate (BDNPP) yielding kinetically relevant pK<sub>a</sub> values of 6.89, 7.37 and 9.00, a K<sub>M</sub> of 10.8  $\pm$  2.1 mM and a k<sub>cat</sub> of 3.20 ( $\pm$  0.38)  $\times 10^{-3}$  s<sup>-1</sup> (at pH 7.5). Attempts to prepare a di-iron analogue resulted in a centrosymmetric dimer, [Fe<sub>2</sub>(BMMHPH)<sub>2</sub>( $\mu$ -OH)<sub>2</sub>](BPh<sub>4</sub>)<sub>2</sub>, with one six-coordinate Fe(III) in each of the  $\alpha$ -sites, connected by two  $\mu$ -hydroxido groups. In this Fe( $\mu$ -OH)<sub>2</sub>Fe diamond core the Fe(III) ions are weakly antiferromagnetically coupled, with  $J = -1.76 \pm 0.03$  cm<sup>-1</sup>. The  $\beta$ -sites were vacant. Attempts to replace the Zn(II) ion with Mg(II) resulted in the formation of a centrosymmetric trimer, *i.e.* [Fe<sub>2</sub>Mg(BMMHPH)<sub>2</sub>(CH<sub>3</sub>COO)<sub>2</sub>(CH<sub>3</sub>O)<sub>2</sub>](BPh<sub>4</sub>)<sub>2</sub>.





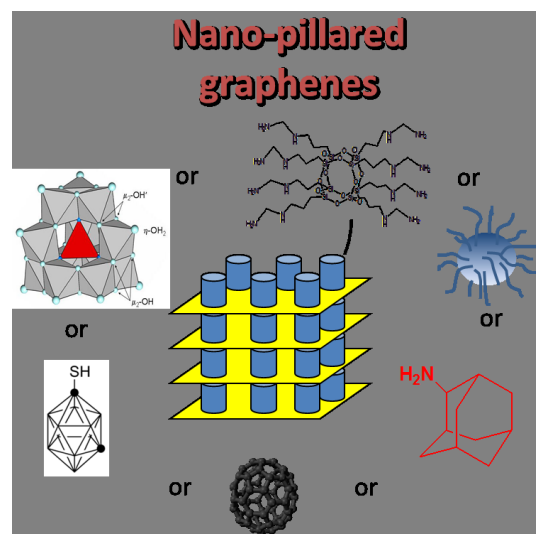
# Graphene Pillaring: Towards Novel Multifunctional Materials

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By taking advantage of the concept of intercalation chemistry and the so-called pillaring method the design and development of novel nanostructured pillared layered materials based on graphene is reported. Various cage-shaped and robust species (see Scheme) such as cubic silsesquioxanes, fullerenes ( $C_{60}$ ), adamantane derivatives, carboranes and alumina (Keggin ion), as well as, organic precursors (amine derivatives) were successfully intercalated into the interlayer space of chemically oxidized graphene (graphene oxide) and graphite nitrate leading to new pillared graphene structures<sup>1-4</sup>. Pillared graphenes were characterized by a combination of powder X-ray diffraction, X-ray photoemission, Raman and FTIR spectroscopies, thermal analysis (DTA/TGA), surface area measurements and microscopy techniques (TEM, SEM, AFM). Representative case studies addressing cutting edge processes of great importance such as the use of these hybrid nanostructures as cytotoxic agents, effective adsorbents for environmental remediation and hydrogen storage materials will be discussed.



- (1) Spyrou, K.; Kang, L.; Diamanti, E. K. et al. *Carbon* **2013**, 61, 313.
- (2) Tsoufis, T.; Tuci, G.; Caporali, S.; et al. *Carbon* **2013**, 59, 100.
- (3) Spyrou, K.; Potsi, G.; Diamanti, E. K.; et al. *Adv. Funct. Mater.* **2014**, 24, 5841.
- (4) Spyrou, K.; Calvaresi, M.; Diamanti, E. K.; et al. *Adv. Funct. Mater.* **2015**, 25, 263.

**Acknowledgments.** This research has been co-financed by the European Union (European Social Fund – ESF) and Greek national funds through the Operational Program "Education and Lifelong Learning" of the National Strategic Reference Framework (NSRF) - Research Funding Program: THALES. Investing in knowledge society through the European Social Fund (no. 377285).



## Octacyanometallates–Versatile Building–blocks for Constructing Multifunctional Molecular Materials

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The d–f metal–organic frameworks (MOFs) containing cyanide bridges, namely 3D assemblies, is being developing slowly as compared with other MOFs.[1] Therefore, this presentation will shortly summarize the synthetic strategies developed so far for designing such molecular assemblies. It will be discussed in detail the own contribution in this field, by presenting the synthetic methodology, the properties of these compounds and the theoretical approaches used for understanding the bonding regime.

An original synthetic strategy has been developed to make cyanide-bridged microporous lanthanide MOFs: it involves the self-assembly of lanthanide building-blocks with octacyanometallates.[2] This method gives 3D networks with highly hydrophilic channels. The resulting MOFs are also robust, enabling repeated dehydration/hydration cycling. This makes them ideal candidates for air drying, water/alcohol separation and proton conduction applications. It will be presented the single-crystal X-ray structure of these materials as well as their adsorption and proton conduction properties, showing that the activated MOFs can adsorb water selectively.

[1].M. Ferbinteanu, F. Cimpoesu, S. Tanase, *Struct. Bond.*, **2015**, 163, 185-230.

[2]. S. Tanase, M. C. Mittelmeijer, G. Rothenberg, C. Mathoniere, V. Jubera, J. M. M. Smits, R. de Gelder *J. Mater. Chem.*, **2011**, 21, 15544-15551.

# Unexpected, Cooperative Spin-Crossover in Iron(II)/Dipyrazolylpyridine Complexes with Large Jahn-Teller Distortions

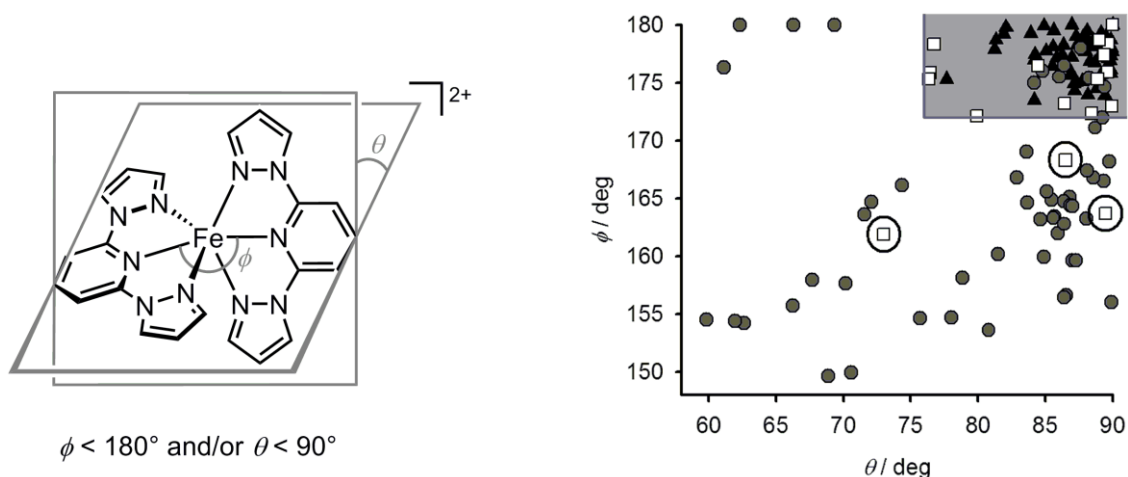
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Derivatives of  $[\text{Fe}(\text{bpp})_2]^{2+}$  (bpp = a 2,6-di{pyrazol-1-yl}pyridine) are widely studied for spin-crossover.[1] However, a complication in their chemistry is that high-spin  $[\text{Fe}(\text{bpp})_2]^{2+}$  complexes often exhibit an angular Jahn-Teller distortion (Figure). This causes a reduction of the trans-N{pyridyl}-Fe-N{pyridyl} angle ( $\phi$ ) below its ideal value of  $180^\circ$ , and/or a twisting of the two tridentate ligands ( $\theta < 90^\circ$ , where  $\theta$  is the dihedral angle between the leastsquares planes of the ligands). Spin-crossover in  $[\text{Fe}(\text{bpp})_2]^{2+}$  derivatives is inhibited if the molecular distortion in their high-spin form is too pronounced. In that case, the structural rearrangement required to interconvert the distorted high-spin and undistorted low-spin states is kinetically inhibited by the rigid solid lattice. Thus many  $[\text{Fe}(\text{bpp})_2]^{2+}$  derivatives that should exhibit spin-crossover, all other things being equal, are spin-crossover inactive in the solid state.

A survey six years ago concluded that only complexes with  $\phi \geq 172^\circ$  and  $\theta \geq 76^\circ$  should be competent to undergo spin-crossover.[1] However, this presentation will describe new compounds that exhibit hysteretic spin-transitions, despite showing significantly larger Jahn-Teller distortions at room temperature (Figure).



**Figure.** The range of Jahn-Teller distortion parameters from compounds that are: low-spin (black triangles); high-spin and spin-crossover active (white squares); high-spin and spin-crossover inactive (gray circles). The distortion range that is normally consistent with spin-crossover activity is shaded, and three anomalous spin-crossover compounds lying outside this range are highlighted.

[1] Halcrow, M. A. *Coord. Chem. Rev.* **2009**, 253, 2493.

## **Synthesis of Benzoquinonoid Radical-Containing Materials with Strong Magnetic Exchange Coupling**

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This presentation will describe our efforts to synthesize molecule-based magnets with strong magnetic exchange coupling by employing benzoquinonoid radical bridging ligands. In particular, a series of tetraazalene radical-bridged dinuclear complexes has been synthesized. Magnetic measurements of these complexes reveals the presence of strong antiferromagnetic exchange between M centers and the ligand radical, with estimated coupling constants of  $J = -620$  (Cr<sup>III</sup>),  $-154$  (Mn<sup>II</sup>),  $-313$  (Fe<sup>II</sup>), and  $-395$  (Co<sup>II</sup>) cm<sup>-1</sup>. The Fe congener behaves as a single-molecule magnet with a spin relaxation barrier of  $U_{\text{eff}} = 52$  cm<sup>-1</sup>. In addition, the synthesis and magnetic properties of a wheel-like cluster comprised of six Mn<sup>II</sup> ions linked by six radical ligands will be discussed. Finally, this presentation will present a new benzoquinonoid-bridged Mn<sup>II</sup> chain compound, which can undergo solid-state ligand-based redox-switching. Structural and resonance Raman spectroscopic characterization for these electron-transfer isomers will be presented.

# Direct Observation of Ultrafast Long-range Charge Separation in Polymer: Fullerene Heterojunctions

Sophia C. Hayes,<sup>1,\*</sup> Françoise Provencher,<sup>2</sup> Nicolas Bérubé,<sup>2</sup> Anthony W. Parker,<sup>3</sup> Gregory M. Greetham,<sup>3</sup> Michael Towrie,<sup>3</sup> Christoph Hellmann,<sup>4</sup> Galatia Pieridou,<sup>1</sup> Michel Côté,<sup>2</sup> Natalie Stingelin,<sup>4</sup> Carlos Silva,<sup>1,5</sup>

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In polymeric semiconductors, charge carriers are polarons, which means that the excess charge deforms the molecular structure of the polymer chain that hosts it. This results in distinctive signatures in the vibrational modes of the polymer. Here, we probe polaron photogeneration dynamics at polymer:fullerene heterojunctions by monitoring its time-resolved resonance-Raman spectrum following ultrafast photoexcitation. We conclude that polarons emerge within 300 fs. Surprisingly, further structural evolution on <50-ps timescales is modest, indicating that the polymer conformation hosting nascent polarons is not significantly different from that near equilibrium. We interpret this as suggestive that charges are free from their mutual Coulomb potential because we would expect rich vibrational dynamics associated with charge-pair relaxation. In contrast, the structure and dynamics following photoexcitation in neat films of the polymer are very different and indicative of excitonic behavior.[1] This is further confirmed from time-resolved resonance-Raman studies and resonance-Raman intensity analysis in solutions of the polymer.

[1] F. Provencher, N. Bérubé, A. W. Parker, G. M. Greetham, M. Towrie, C. Hellmann, M. Côté, N. Stingelin, C. Silva, and S. C. Hayes, *Nat. Comm.* **2014**, 5, 4288.

# Dendritic Maleimide Functionalization of Core-shell ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/polymer) Nanoparticles for Efficient Bio-immobilization

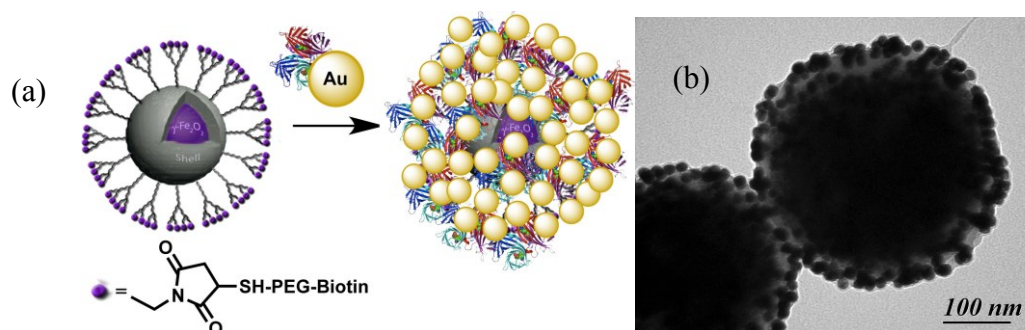
K. Heuzé,<sup>\*a</sup> L.Mitcova,<sup>a</sup> H.Rahma,<sup>a</sup> T.Buffeteau,<sup>a</sup> R.Clérac,<sup>b</sup> L.Vellutini<sup>a</sup>

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A new route for the preparation of stable and water-dispersible MNPs has been developed in order to ensure a selective and covalent immobilization of biomolecules using maleimide-thiol coupling chemistry.[1]An extremely high maleimidefunctionalization of core-shell  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/Polymer MNPs was achieved by grafting dendritic coupling agent *via* a convergent approach. The efficiency of the grafted MNPs, for the immobilization of biomolecules has been successfully demonstrated with nanoscalebio-markersand was estimated at 280 pmol/mg of MNPs (Figure 1). The magnetic properties of the maleimide functionalized MNPs display virtually identical superparamagnetic properties as native nanoparticles, confirming that the magnetic core of the nanoparticles remains intact after functionalization. This is of crucial importance since many applications of NMPs require the integrity of their magnetic properties after chemical surface modification.



**Figure 1.**(a) Immobilization of nanoscalebio-markersonto maleimide functionalized MNPs. (b) corresponding TEM image.

The engineering of functional surfaces remains one of the keys for optimizing immobilization of biomolecules. Therefore, our strategy using maleimide functional group opens a broad field of applications in biomedicine as this type of functionalization is highly relevant for targeting, imaging, detection, diagnostic and therapeutic applications. Moreover, our synthetic strategy can be readily extended to other functional groups efficient for bioconjugation applications and more generally for bionanotechnology.

[1] L.Mitcova, H.Rahma, T.Buffeteau, R.Clérac, L.Vellutini, K.Heuzé, *submitted*, **2015**.

# New Oxime Ligands in the Chemistry of Polynuclear Metal Complexes

M. Holyńska

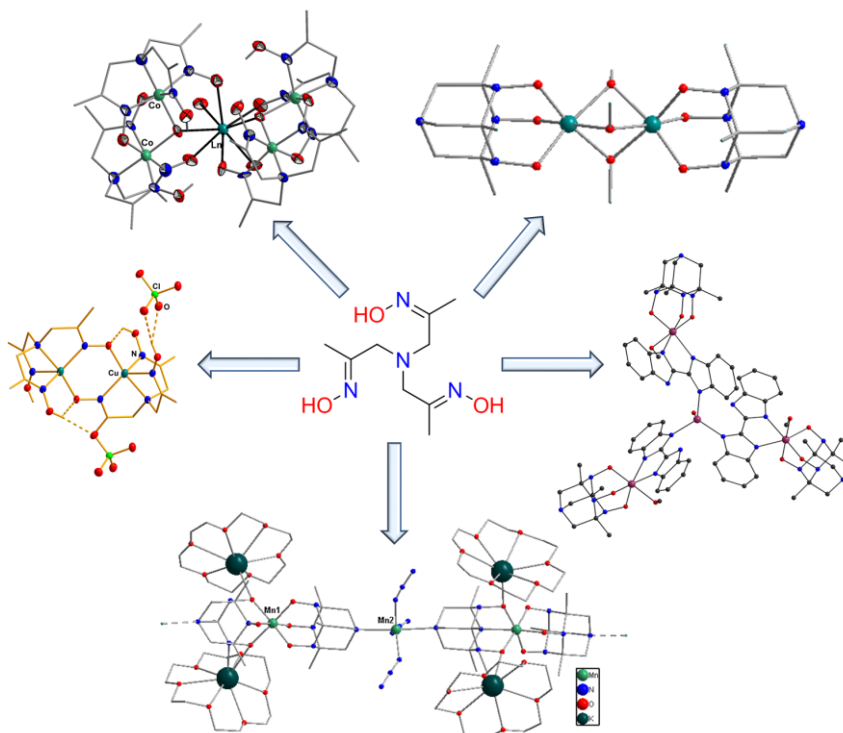
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Metal complexes with oxime ligands continue surprising with their unexpected molecular architectures. Recent advances include new approaches to link oxime-bridged clusters [1].

Coordination of metal ions often imposes a catalytic effect leading to unusual rearrangements within the organic ligands molecules [2]. In particular, the oxime  $\text{--C=N-OH}$  moiety can undergo addition with nucleophilic reagents attacking the C atom and electrophilic reagents reacting with the polarized  $\text{C=N}$  bond [2].

In this contribution I will introduce a particular class of flexible tripodal oxime ligands capable of intramolecular cyclization to yield tetraazaadamantane derivatives and explore their reactivity (Figure 1).



**Figure 1.** Variety of products derived from the tris(2-hydroxyiminopropyl)amine ligand.

[1] A. M. Mowson, T. N. Nguyen, K. A. Abboud, G. Christou, *Inorg. Chem.*, **2013**, *52*, 12320.

[2] V. Duros, H. Sartz, S. J. Teat, Y. Sanakis, O. Roubeau, S. P. Perlepes, *Inorg. Chem. Commun.*, **2014**, *50*, 117.

# Nanocomposite Copolymer Films Characterized by Long-range Domain Order

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Nanocomposite structures comprising of long-range ordered copolymer matrix and nanoparticles (NPs) are increasingly drawing attention due to their abilities to self-assembling [1]. This thermodynamically driven process may lead to an ordered organization of embedded NPs and solve aggregation issues. Moreover, this bottom-up approach belongs to a very promising, low-cost lithographic methods and is expected to play an important role in semiconductor industry. The self-assembling systems exhibit perfect periodicity in the microscale and can produce the feature size less than 10 nm which outclasses standard photolithographic techniques. However, coherently ordered grains are relatively small and fabrication of a long-range crystalline and defectless order remains problematic. In order to overcome this issue we adopted the method introduced by S. Park [2] producing specific sapphire substrates as a templates for polymeric films. Single-crystalline wafers, such as sapphire, have to be cut along specific crystallographic planes in order to produce unstable surfaces which upon heating reconstruct, generating crystal facets that form a sawtooth topography, where the orientation of the ridges formed by the sawtooth persist over the entire surface (Fig1 a). Prepared substrate is then ready for copolymer film deposition via spin coating. Solvent-annealing leads to morphological motives buildup which run parallel to the edges of the facets. This preferential orientation minimizes perturbations of the lateral packing of the block copolymer chains and results in long-range crystalline order over macroscopic wafer surfaces (Fig1 b).

Copolymer domain structures were investigated using atomic force microscopy (AFM) and MicroRaman spectrometry. Moreover, nuclear magnetic resonance (NMR) spectroscopy with spin diffusion experiment was applied in order to assess both, domains and interfacial dimensions.

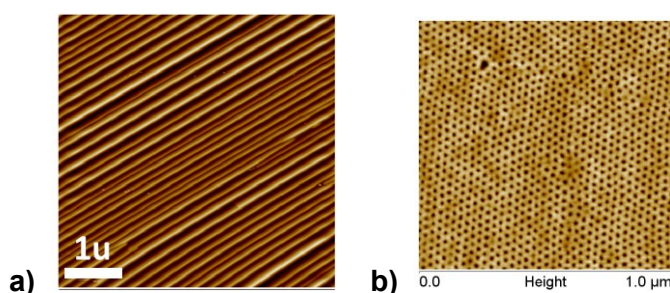


Fig. 1 AFM images: a) sawtooth topography of sapphire surface, b) hexagonally ordered cylindrical structures of PEO formed in PS matrix via self-assembling phenomenon.

[1] T. Smart, H. Lomas, M. Massignani, M.V. Flores-Merino, L.R. Perez, G. Battaglia, 3 (2008) Nanotoday

[2] S. Park, D.H. Lee, J. Xu, B. Kim, S.W. Hong, U. Jeong, T. Xu, T.P. Russell, 323 (2009) Science

Acknowledgement: This work was supported by the National Science Centre under research Grant no 2013/11/B/ST3/04190 (Contract no. DEC-2013/11/B/ST3/04190).



## Magnetic Porous Carbon Nanocomposites as Adsorbents and Catalysts for Environmental Remediation

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In the present work, mesoporous carbon-based nanocomposites were prepared using as carbon source, sugar, spent-coffee waste and expanded starch. These porous matrices were decorated with Fe<sup>0</sup>, magnetite and  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles. The nanocomposites were developed by *in-situ* reduction of dispersed Fe<sup>3+</sup> ions onto the porous carbon matrices. The samples were studied with a combination of characterization techniques such as powder X-ray diffraction (XRD), Fourier-transform infrared (FT-IR) and Mössbauer spectroscopy, N<sub>2</sub> adsorption measurements, transmission electron microscopy (TEM), magnetization measurements, and thermal analysis methods. Analysis of the results have revealed first, the characteristics of the host structure and second the formation of uniform nanosized iron based particles inside the pore system with high magnetic species loading, whereas Mössbauer spectroscopy and magnetic measurements in low temperatures confirm their nature. Kinetic studies were performed and it was shown that there is a rapid sorption of Cr(VI) ions in the presence of the reported nanocomposites, and a better adsorption capacity per unit mass of sorbent in comparison to that of pristine carbons. The results indicate highly pH-dependent sorption efficiency of the nanocomposites, whereas their kinetics were described by a pseudo-second-order kinetic model.

# The Role of Aluminum Coordination & Water Mobility in Y Nanozeolites: A High Temperature NMR Study

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In this work the unique physicochemical properties of a synthesized HY nanozeolite during thermal dehydration are presented. The nanozeolite displays a remarkable architecture, comprised of a mixture of well crystalized ultrathin platelets and octahedral nanocrystals (<100nm), dressed with penta-coordinated extra-framework Al<sup>(V)</sup>. HRTEM measurements in combination with <sup>27</sup>Al MAS NMR and <sup>1</sup>H NMR relaxation measurements performed in the temperature range 20-600°C, show that despite excellent crystallinity, framework Al<sup>(IV)</sup> bonding in the nanozeolite is strongly distorted at atomic scale, while extra-framework Al<sup>(V)</sup> sites induce a significant polarization field, which influences strongly the coordination of polar molecules such as water [1]. As a consequence, water protons in the nanozeolite attain two different mobility (interaction) states: (i) water molecules interacting strongly with Al<sup>(V)</sup> acquiring high <sup>1</sup>H NMR T<sub>1</sub>/T<sub>2</sub> ratio, and (ii) fast exchanged protons belonging to water molecules in proximity with Al<sup>(IV)</sup> and Al<sup>(VI)</sup> sites with low T<sub>1</sub>/T<sub>2</sub> ratio.

Important findings of this work are: (i) framework Al<sup>(IV)</sup> in the nanozeolite is astonishing resilient to thermal dehydration when compared to Al<sup>(IV)</sup> in bulk HY zeolites which degrades quickly by heating, due to dealumination. A similar effect has been observed in Al-exchanged Y zeolites also rich in Al<sup>(V)</sup>; (ii) extra-framework Al<sup>(VI)</sup> in the nanozeolite is converted to Al<sup>(V)</sup> by heating, while in the bulk zeolite Al<sup>(VI)</sup> is observed to increase with heating (observed with <sup>27</sup>Al 3Q MAS analysis); (iii) a final important conclusion is that water protons appear to interact very strongly with the solid matrix in the nanozeolite, probably due to the presence of a polarization field induced by the Al<sup>(V)</sup> [1]. These properties unveil the very important role of the Al<sup>(V)</sup> decoration in this nanozeolite.

[1] Huang J., Jiang Y., Marthala V. R. R., Thomas B., Romanova E., Hunger M.; *J. Phys. Chem. C*, **2008**, 112 (10), 3811-3818.

# Liquid Crystalline Derivatives of $\pi$ -delocalized Radicals

Piotr Kaszyński

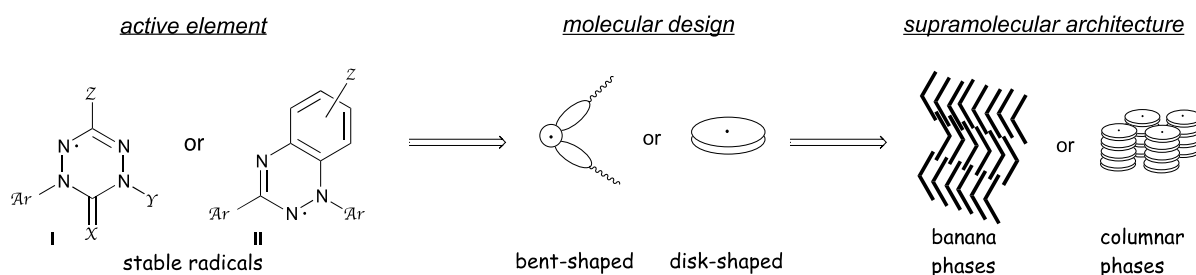
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Open-shell organic systems are becoming increasingly important structural elements of advanced materials for spintronics, memory and energy storage, photomagnetic devices, and energy harvesting. In this context, we have been studying supramolecular assemblies of stable  $\pi$ -delocalized radicals. Recently, we focused on the verdazyl and benzo[1,2,4]triazinyl systems, which upon substitution with appropriate elongated or wedge-shaped groups give anisometric bent-core or disk-like derivatives.

Synthesis, liquid crystalline, optical, electrochemical, photovoltaic and magnetic results will be presented and discussed.



## References

1. Jankowiak, A.; Pocięcha, D.; Szczytko, J.; Monobe, H.; Kaszyński, P. *J. Am. Chem. Soc.* **2012**, *134*, 2465-2468; Jankowiak, A.; Pocięcha, D.; Monobe, H.; Szczytko, J.; Kaszyński, P. *Chem. Commun.* **2012**, 7064-7066.
2. Jasinski, M.; Gerding, J. S.; Jankowiak, A.; Gebicki, K.; Romanski, J.; Jastrzebska, K.; Sivaramamoorthy, A.; Mason, K.; Evans, D. H.; Celeda, M.; Kaszyński, P. *J. Org. Chem.* **2013**, *78*, 7445-7454.
3. Jankowiak, A.; Pocięcha, D.; Szczytko, J.; Monobe, H.; Kaszyński, P. *J. Mater. Chem. C*, **2014**, *2*, 319-324.
4. Bodzioch, A.; Zheng, Z.; Kaszyński, P.; Utecht, G. *J. Org. Chem.* **2014**, *79*, 7294-7310.
5. Jasinski, M.; Pocięcha, D.; Monobe, H.; Szczytko, J.; Kaszyński, P. *J. Am. Chem. Soc.* **2014**, *136*, 14658-14661.

# Electronic and Magnetic Properties of Mn Doped ZnO Nanocrystal

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Mn doped ZnO nanocrystals with different percentage of Mn contents were synthesized by a simple solvo-thermal method. The change of volume ratios of the co-surfactants creates  $\text{Zn}_{1-x}\text{Mn}_x\text{O}$  nanoparticles with various shapes ranging from quasi-spheres to hexagonal pyramids to irregular shapes as well as controlling the dopant amounts of the nanoparticles. The successful incorporation of  $\text{Mn}^{2+}$  into the ZnO was supported through the XRD, EDX, and EPR. XRD spectra show that all the samples are hexagonal wurtzite structures. The X-band EPR spectrum of the  $\text{Zn}_{0.997}\text{Mn}_{0.003}\text{O}$  taken at 298 K exhibits the characteristic six line hyperfine structure of the  $^{55}\text{Mn}$  nuclear spin. The  $\text{Zn}_{0.997}\text{Mn}_{0.003}\text{O}$  nanocrystal shows the typical superparamagnetic behavior, in the temperature dependence of magnetization and its reverse M in which the magnetization is gradually increased with the decreasing temperature. The first-principles density functional calculation is used to investigate the electronic structures and magnetic properties of Mn-doped and bulk ZnO. The band structure calculation shows that the band gaps of Mn doped ZnO (0.03 % of Mn) is narrower than the band gap of the bulk with wurtzite structure.

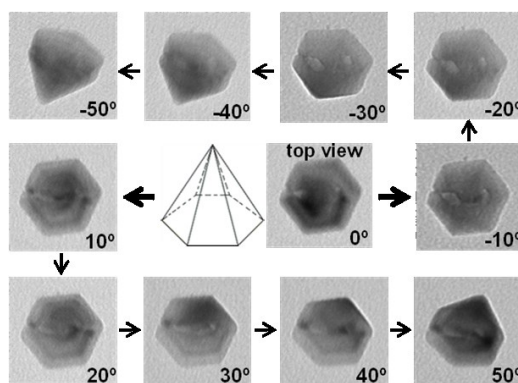


Fig. 1. Tilted TEM images of a single hexagonal pyramid Mn doped ZnO nanocrystal.

## A Microporous Cobalt and Iron Metal Organic Framework with Isonicotinic Acid

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The last decade there has been a tremendous research interest in the construction of metal-organic frameworks (MOFs) mainly because of their intriguing architectures and novel physical properties that lead to potential applications in a series of areas including gas storage and separation, catalysis, magnetism, sensing, etc.<sup>1,2</sup> Microporous MOFs containing an appreciable internal surface area and flexible chemical composition have attracted particular concern since they are strong candidates for use in the adsorption and storage of gases of environmental interest such as H<sub>2</sub>, CH<sub>4</sub> and CO<sub>2</sub>. Selective trapping of CO<sub>2</sub> from air or the emission of coal-fired power plants under ambient conditions is a main priority for many research groups. Currently, several methods are used for this purpose, however many of them involve a high energy penalty and are inefficient in terms of releasing adsorbed CO<sub>2</sub> molecules. Thus, alternative methods have been proposed, with many including a range of porous materials. Among the various classes of the latter, MOFs are possibly the most promising ones for this goal due to their high surface areas, adjustable and ordered structures, open metal sites and low density.<sup>3,4</sup> We herein report a new MOF {[Co<sub>9</sub>(INA)<sub>18</sub>(H<sub>2</sub>O)<sub>6</sub>]<sup>-</sup>·11DMF·15H<sub>2</sub>O}<sub>∞</sub> denoted as Co<sub>9</sub>-INA (INA<sup>-</sup>= the anion of isonicotinic acid) that was prepared from the combination of HINA and Co(NO<sub>3</sub>)<sub>2</sub> in DMF/H<sub>2</sub>O under solvothermal conditions.<sup>5</sup> Co<sub>9</sub>-INA exhibits a rigid 3D-porous structure with interesting structural and novel topological features. Co<sub>9</sub>-INA shows an appreciable BET area (910 m<sup>2</sup> g<sup>-1</sup>), the highest among the known Co-INA MOFs, and significant CO<sub>2</sub> uptake (4.2 at 273 K/1 bar) and selectivity over CH<sub>4</sub> (6.7 at zero coverage and 273 K). Moreover, Co<sub>9</sub>-INA displays a remarkable capability to undergo single-crystal-to-single-crystal (SCSC) transformations involving insertion/removal of guest solvent molecules.

(1) Férey, G. Chem. Soc. Rev. 2008, 37, 191-214.

(2) (a) Bradshaw, D.; Claridge, J. B.; Cussen, E. J.; Prior, T. J.; Rosseinsky, M. J. Acc. Chem. Res. 2005, 38, 273-282. (b) Eddaoudi, M.; Moler, D. B.; Li, H. L.; Chen, B. L.; Reineke, T. M.; O'Keeffe, M.; Yaghi, O. M. Acc. Chem. Res. 2001, 34, 319-330.

(3) (a) Bourrelly, S.; Llewellyn, P. L.; Serre, C.; Millange, F.; Loiseau, T.; Férey, G. J. Am. Chem. Soc. 2005, 127, 13519-13521. (b) Torrisi, A.; Bell, R. G.; Mellot-Draznieks, C. Cryst. Growth Des. 2010, 10, 2839-2841. (c) Ramsahye, N. A.; Maurin, G.; Bourelly, S.; Llewellyn, P.; Serre, C.; Loiseau, T.; Devic, T.; Férey, G. J. Phys. Chem. C 2008, 112, 514-520. (d) Nelson, A. P.; Farha, O. K.; Mulfort, K. L.; Hupp, J. T. J. Am. Chem. Soc., 2009, 131, 458-460

(4) Li, J.R.; Ma, Y.; McCarthy, M. C.; Sculley, J.; Yu, J.; Jeong, H.-K.; Balbuena, P. B.; Zhou, H.-C. Coord. Chem. Rev. 2011, 255, 1791-1823.

(5) Kourtellaris, A.; Moushi, E.E.; Spanopoulos, I.; Manos, M. J.; Papaefstathiou, G. S.; Trikalitis, P. N.; Tasiopoulos, A. J. A. Cryst. Growth Des., 2015, 15 (1), 185-193

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**Magnetostructural Correlations in M(II), M = Fe, Co, Ni and Mn(III)  
Complexes Bearing the  $[R_2P(E)NP(E)R_2]^-$  Chelating Ligands,  
E = O, S, Se; R = Ph, <sup>i</sup>Pr**

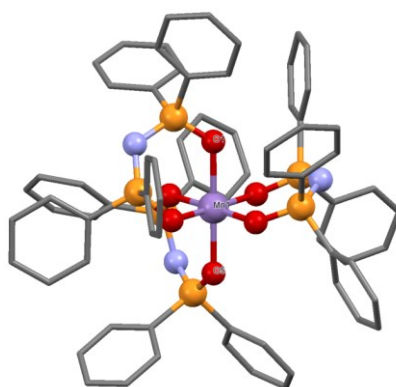
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Coordination of the  $[R_2P(E)NP(E')R'_2]^-$  chelating ligands, E = O, S, Se; R = Ph, <sup>i</sup>Pr, to various transition metal ions has afforded an extensive range of complexes exhibiting different structures and coordination environments.[1] Magnetostructural correlations have been recently explored for tetrahedral Fe(II) (S=2), Co(II) (S=3/2) and Ni(II) (S=1), as well as for octahedral Mn(III) (S=2) and Ni(II) (S=1) complexes bearing the above type of ligands. These complexes have been investigated by X-ray crystallography, magnetometry, various spectroscopic techniques (EPR, Mössbauer, far-IR magnetic) and computational methods, in successful collaboration with other research groups. First and second coordination sphere effects on the magnetic properties of the above systems will be discussed. The octahedral S=2  $[Mn\{(OPPh_2)_2N\}_3]$  complex (Fig. 1), containing a Mn(III)O<sub>6</sub> core, exhibits slow relaxation of magnetization in the presence of magnetic fields.[2]

We would like to thank all our collaborators (acknowledged in the talk) for their invaluable contribution to this work, as well as the Special Research Account of the University of Athens and the Fulbright Foundation in Greece for financial support.



**Figure 1.** The crystal structure of  $[Mn\{(OPPh_2)_2N\}_3]$ . [2]

[1] C. Silvestru, J.E. Drake, *Coord. Chem. Rev.* **2001**, 223, 117.

[2] A. Grigoropoulos, M. Pissas, P. Papatolis, V. Psycharis, P. Kyritsis, Y. Sanakis, *Inorg. Chem.* **2013**, 52, 12869.

# Copper(II) and Copper(II)/Lanthanide(III) Coordination Clusters and Polymers Based on Oxime Ligands and Di-2-pyridyl Ketone- Novel Organic Ligand Transformations

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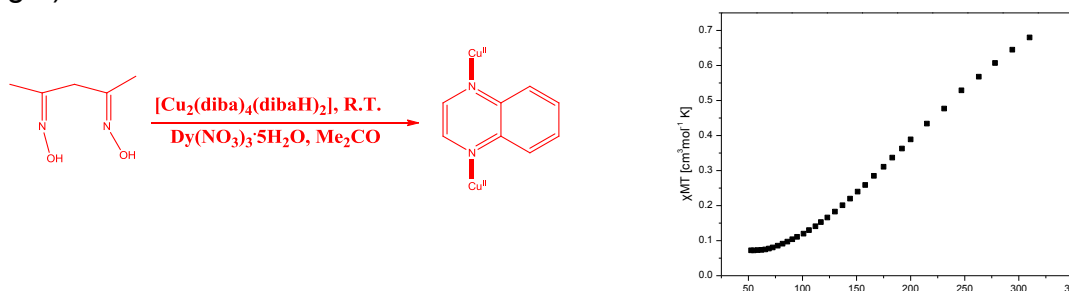
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Transition- and mixed transition/lanthanide-metal coordination clusters continue to attract the intense interest of inorganic chemists due to their involvement in many areas of basic and applied research [1-3]. A central theme in our laboratories is the synthesis and characterization of 3d- and 3d/4f-metal complexes. We have been using a variety of ligand families in our efforts, including di-2-pyridyl ketone (dpk), 2-pyridyl oximes and aliphatic dioximes. In our short talk we shall describe reaction schemes that lead to Cu<sup>II</sup> and Cu<sup>II</sup>/Ln<sup>III</sup> (Ln= lanthanide) clusters and polymers based on the above mentioned ligands together with their preliminary characterization (Fig.1).



**Figure 1.** A simplified view of the transformation of the 2,4-pentanedione dioxime to quinoxaline (qunx, left) upon coordination and the  $\chi_M T$  vs  $T$  (right) data for the 1D {[Cu<sub>2</sub>(diba)<sub>4</sub>(qunx)]}<sub>n</sub> polymer.

This work was supported by the ARISTEIA Action (project code 84, acronym MAGCLOPT) of the Operational Programme “Educational and Lifelong Learning”, co-funded by ESF and National Resources (to S. P. P.).

- [1] R. Bagai and G. Christou, *Chem. Soc. Rev.* **2009**, 38, 1011.
- [2] R. Sessoli and A.K. Powell, *Coord. Chem. Rev.* **2009**, 253, 2328.
- [3] C. J. Milios and R.E.P. Winpenny, *Struct. Bonding* **2015**, 164, 1.

# Synthesis and Photophysical Properties of New Lanthanide Metal-Organic Frameworks

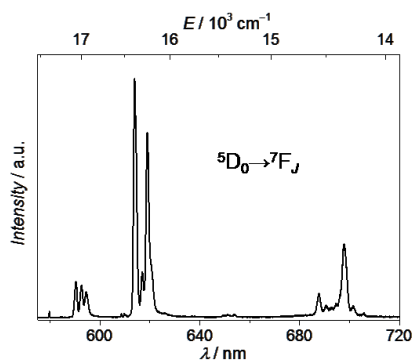
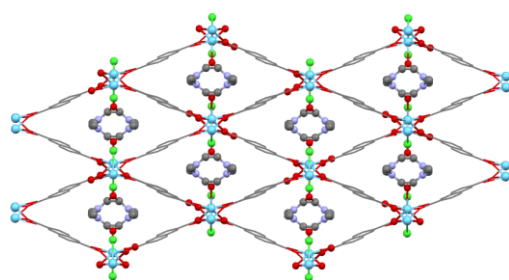
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Luminescent lanthanide Metal-Organic Frameworks combine the unique luminescence characteristics of lanthanide ions (high luminescence quantum yield, long-lived emission, large Stokes shifts and characteristically sharp emission peaks) with the permanent porosity and guest binding ability of MOFs thus making them a highly interesting class of hybrid materials.[1]

In this contribution we present the synthesis, crystallographic characterization and photophysical study of three series of LnMOFs with 2,6-naphthalene dicarboxylate (2,6-NDC) 2-hydroxy terephthalic acid and 2-methoxy terephthalic acid as ligands. In the case of 2,6-NDC we obtain a previously unreported 3D structure, while the other two ligands yield a 3D structural motif already reported by Reedijk et. al [2]. The majority of the MOFs show emission from the  $\text{Ln}^{3+}$  ion, upon selective excitation of the bridging ligand, at wavelengths ranging from the visible to the near infrared region. The emission properties are discussed in terms of the electronic properties of the bridging ligands.



[1] Y. Cui, B. Chen, G. Qian, *Coord. Chem. Rev.*, **2014**, 273-274, 76.

[2] C. A. Black, J. S. Costa, W. T. Fu, C. Massera, Olivier Roubeau, S. J. Teat, G. Aromí, P. Gamez, J. Reedijk, *Inorg. Chem.*, **2009**, 48, 1062.



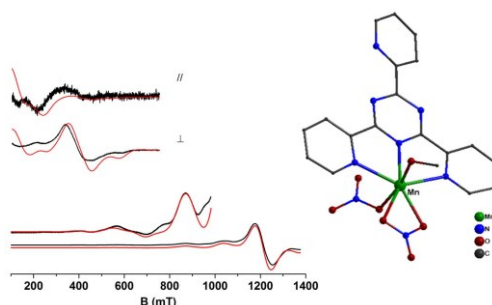
# Seven Coordinate Pentagonal Bipyramidal Mononuclear Mn(II) Complexes

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Manganese complexes have long been investigated because of their role in biological and chemical catalysis, including the light driven oxidation of water to dioxygen in Photosystem II. One of the most important aspects concerning the functional properties of Mn in these systems is the role of the coordination number. Relevant to this issue are correlations of spectroscopic parameters such as the zero field splitting (zfs) with the coordination number as well as the nature of the ligands. Among the various oxidation states in which Mn is encountered, in the present talk we focus on the Mn(II)( $S=5/2$ ) ion. During the last years there have been many studies concerning six- and five- but only few seven- coordinate Mn(II) complexes [1]. We have synthesized and structurally characterized several novel seven coordinate mononuclear Mn(II) complexes with N/O ligands. We determine the zfs parameters by X and Q-band EPR spectroscopy and compare the experimental values with those derived by Density Functional Theory (DFT) calculations.



**Figure 1.** Room temperature dual mode X band and perpendicular mode Q band EPR spectra and crystal structure of a seven coordinate Mn(II) complex.

## Acknowledgments

This work was performed in the framework of "Advanced Materials and Devices for Collection and Energy Management" project within GSRT's KRIPIS action, funded by Greece and the European Regional Development Fund of the European Union under NSRF 2007-2013 and the Regional Operational Program of Attica

[1] J. Rich, C. E. Castillo, I. R. M. Rodriguez, C. Duboc, M.-N. Collomb, *Eur. J. Inorg. Chem.* 2010, 3658-3665.

# Surface Chemistry on Recycled Carbon Materials: Single-Site Heterogeneous Catalysts and Applications

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Pyrolytic char is one of the main products obtained after the pyrolysis process for disposing of waste tyres. It has contiguous structure with carbon black and this confers on it the general properties of carbonaceous materials such as thermal stability, high corrosion resistance in acid/base and low cost [1].

Our synthetic strategy presented here for covalent anchoring of Mn-catalysts onto pyrolytic carbon uses silylation reaction of appropriate ligand-silane-precursors with surfacial –OH groups of the oxidized pyrolytic carbon achieved by nitric acid ( $\text{HNO}_3$ ) [2]. This study refers a) to the synthetic process for the development of single-site heterogeneous catalysts using as support matrix the surface of recycled carbon from tyres and b) to the investigation of the behavior of active pyrolytic carbon as catalyst support material for grafted non-heme manganese complexes. The developed Mn-catalysts were evaluated i) in epoxidation reactions of alkenes with hydrogen peroxide and ammonium acetate as co-catalyst and ii) in oxidative degradation of sulphonated azo dye, methyl orange (MO) in the presence of  $\text{NaIO}_4$  [3]. The present catalytic data obtained by Mn-catalysts grafted onto pyrolytic carbon from recycled tyres were compared to those obtained by using commercial activated carbon as support material of the same Mn-catalysts. The catalytic mechanism for alkene epoxidation and a full mapping of the catalytic degradation of MO and product formation will be given.

[1] J.L. Allen, J.L. Gatz, P.C. Eklund, *Carbon*, **1999**, 37, 1487.

[2] A. Mavrogiorgou, M. Papastergiou, Y. Deligiannakis, M. Louloudi, *J. Mol. Catal. A* **2014**, 393, 8.

[3] E. Seristatidou, A. Mavrogiorgou, I. Konstantinou, Y. Deligiannakis, M. Louloudi, *J. Mol. Catal. A* **2015**, 403, 84.

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## **Nanospace within Metal-Organic Frameworks: Plenty of Opportunities for Heterogeneous Catalysis**

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Metal-organic frameworks (MOFs) represent a new class of materials, and one of their striking features lies in the tunable, designable, and functionalizable nanospace. The nanospace within MOFs allows designed incorporation of different functionalities for targeted applications, such as gas storage/separation, sensing, drug delivery; and it has also provided plenty of opportunities for heterogeneous catalysis application. We will illustrate different approaches to develop MOFs as heterogeneous catalysts for epoxidation, CO<sub>2</sub> fixation, and fixed-bed reactions.

# Alkaline Earth Metal Ion/Dihydroxy-Terephthalate MOFs: Structural Diversity and Unusual Luminescent Properties

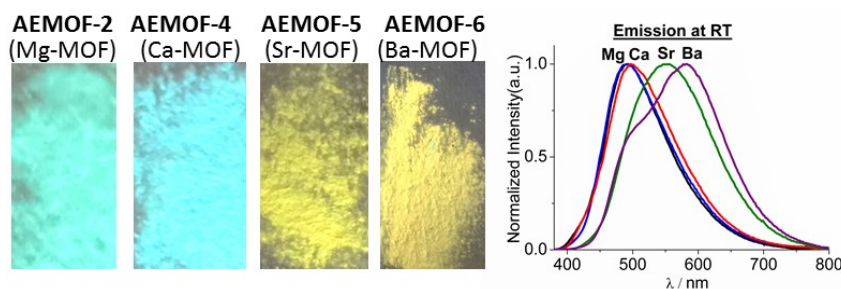
M. J. Manos,<sup>\*a</sup> A. Douvali,<sup>a</sup> T. Lazarides,<sup>b</sup> A. Tsipis,<sup>a</sup> S. Eliseeva,<sup>c</sup> S. Petoud,<sup>c</sup> G. S. Papaefstathiou,<sup>d</sup> A. Hatzidimitriou,<sup>b</sup> C. D. Malliakas,<sup>e</sup> M. G. Kanatzidis,<sup>e</sup> M. P. Gullo,<sup>f</sup> A. Barbieri,<sup>f</sup> I. Margiolaki,<sup>g</sup> I. Papadas,<sup>h</sup> G. S. Armatas<sup>h</sup>

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Metal Organic Frameworks (MOFs) based on alkaline-earth (group 2) ions (**AEMOFs**) have received much less attention compared to those of transition metal ions, with the Sr<sup>2+</sup> and Ba<sup>2+</sup> MOFs being still scarce.

Herein, we present a series of **AEMOFs (AEMOFs-1-6)** based on the H<sub>2</sub>dhtp<sup>2-</sup> ligand (H<sub>4</sub>dhtp=2,5-dihydroxy-terephthalic acid). The reported MOFs display structural variety with diverse topologies and new structural features. **AEMOFs** exhibit interesting and unusual luminescent properties including a strong dependence of emission wavelength on the alkaline earth metal ion (red shifted emission with heavier alkaline earth metal ions, **Figure 1**) and a bathochromic shift of their emission at low temperature (77 K). Remarkably, **AEMOF-1** was found extremely capable for detection, via a luminescence “turn-on” sensing mechanism, of trace water concentrations in various organic solvents and in fact, represents the first MOF showing such sensing capability. [1] Furthermore, **AEMOF-6** (first example of a Ba<sup>2+</sup> MOF with the H<sub>2</sub>dhtp<sup>2-</sup> ligand) displays rare yellow fluorescence at room temperature, which is attractive for solid state lighting applications.



**Figure 1.** The alkaline earth metal ion-dependency of the luminescence properties of the reported MOFs [Photos: Emission of crystals of **AEMOF-2**, **4**, **5** and **6** compounds crushed on a filter paper and irradiated with a standard laboratory UV lamp ( $\lambda_{\text{exc}} = 360 \text{ nm}$ )].

[1] A. Douvali, A. C. Tsipis, S. V. Eliseeva, S. Petoud, G. S. Papaefstathiou, C. D. Malliakas, I. Papadas, G. S. Armatas, I. Margiolaki, M. G. Kanatzidis, T. Lazarides, M. J. Manos, *Angew. Chem. Int. Ed.* **2015**, 54, 1651.

## Oxalamide Based Metal-Organic Frameworks

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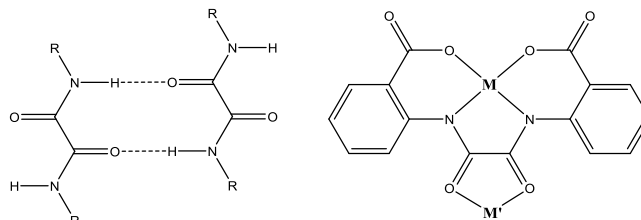
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The oxalamide moiety has been largely utilized within the realm of Crystal Engineering due to its ability to form strong hydrogen bonds. Oxalamides are capable of receiving and donating two self-complementary intermolecular hydrogen bonds either in the solid-state or in solution and that results in a peculiar self-organization. The hydrogen bonding between oxalamides has been utilized to structurally pre-organize diacetylenes for their topochemical polymerization.[1]

Depending on the nature of the substituents on the oxalamide moiety and the degree of the deprotonation of the N-H groups, oxalamides may chelate to metal ions enabling the two C=O bonds to chelate to a second metal ion. This strategy has been utilized to construct molecular-based compounds exhibiting a spontaneous magnetization.[2]



**Figure.** Aspects of oxalamide chemistry.

Herein we will present our efforts to synthesize a series of polycarboxylate ligands bearing an oxalamide backbone and their use in constructing metal-organic frameworks (MOFs) with them. Such MOFs may either have their interiors decorated with the oxalamide moiety or chelate a metal ion, thus enhancing their ability to recognize and / or sense guest molecules or ions.

[1] Kane, J.J.; Liao, R.-F.; Lauher, J.W.; Fowler, F.W.J. *Am. Chem. Soc.*, **1995**, *117*, 12003.

[2] Nakatani, K.; Carriat, J. Y.; Journaux, Y.; Kahn, O.; Lloret, F.; Renard, J. P.; Pei, Y.; Sletten, J.; Verdaguer, M. *J. Am. Chem. Soc.*, **1989**, *111*, 5739.

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## Looking for Photomagnetic Single Molecule Magnets

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The rational design of molecule-based systems displaying tunable optical and/or magnetic properties under external stimuli has received a great deal of attention recently. This interest is driven by the potential applications in the high-performance molecule-based electronic devices in the area of recording media, switches, sensors, and displays. As examples, Fe(II) complexes and cyanido-bridged compounds notably demonstrate the concomitant change in magnetic and optical properties by thermally and light-induced spin crossover or metal-to-metal electron transfer respectively [1,2].

Since several years, we explore the possibility to combine the electronic switching with a magnetic bistability, as shown by the well-known Single Molecule Magnets. In this presentation, we will discuss about two different strategies to reach this objective. The first strategy is devoted to a building block approach that allows to build materials with Fe(II) electron transfer or spin crossover units and Mn(III) Single-Molecule Magnets linked by cyanido bridges [3, 4]. The second strategy is to look for spin crossover Fe(II) complexes with a single-ion magnetic anisotropy big enough to induce Single-Molecule Magnet properties at low temperature [5,6].

### References:

- [1] S. Decurtins et al., *Chem Phys. Lett.* **1986**, 1, 105.
- [2] O. Sato et al., *Science* **1996**, 272.
- [3] R. Ababei, C. Pichon, O. Roubeau, Y. Li, N. Bréfuel, L. Buisson, P. Guionneau, C. Mathonière and R. Clérac *J. Am. Chem. Soc.*, **2013**, 135, 14840.
- [4] R. Ababei, Y.-G. Li, M. Kalisz, O. Roubeau, C. Coulon, E. Harté, X. Li, C. Mathonière and R. Clérac *New. J. Chem.*, **2009**, 33, 1237.
- [5] X. Feng, I.-R. Jeon, M. Rouzières, Andrew Ozarowski, M. L. Aubrey, M. I. Gonzalez, R. Clérac and J. R. Long *J. Am. Chem. Soc.*, **2013**, 135, 15880.
- [6] C. Mathonière, H.-S. Lin, D. Siretanu, R. Clérac and J. Smith *J. Am. Chem. Soc.*, **2013**, 135, 19083.

# **A Review of Hydrocarbon Exploration in Western Greece and its Potential**

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The Ionian Zone in western Greece is a possible hydrocarbon producing area. Oil seeps are abundant in the area and the zone is a continuation of the Albanide tectonic zones with active oil fields. The Ionian Zone is composed of Triassic evaporites and carbonates that are overlain by Jurassic-Cretaceous carbonates and Cretaceous-Tertiary clastics. The units under the evaporites are believed to host the most attractive plays in the area. However, these units have never been reached. Tectonic movements in Miocene to Pliocene times have a serious effect on this lithology and the role of the evaporites in the tectonics is highly underlined. Maturity modeling shows that the units under the evaporites produce hydrocarbons and hence comprehensive studies aiming to target these plays are more than essential.

One exploration well, drilled in 2002, experienced severe overpressures and hence deep drilling was not encouraged. Variable explanations are listed, one of them is the possibility of hydrocarbon reservoirs.



**Figure.** The last exploration well in Greece, Demetra-1, Epeirus.

The exploration history in Greece reveals that foreign explorers were interested but unorthodox drilling, scarcity of planning, delays and unprofessionalism has a negative impact to the upstream Greek industry. Greece is the only country in the Mediterranean area without any drilling activity since 2002.

More studies are important for the Ionian Zone. These studies must trace the deep evaporitic strata and target areas where the evaporites will be fully penetrated. Drilling in western Greece should continue, there are some 25 oil and gas fields in Albania and only one discovery has been made so far in western Greece (west Katakolon). This is highly significant as it proves the existence of a viable play and its continuation throughout western Greece. It is evident for obvious economic and scientific purposes that a new drilling era should begin in the near future. It is so profound the advantages of such activity for the Greek economy

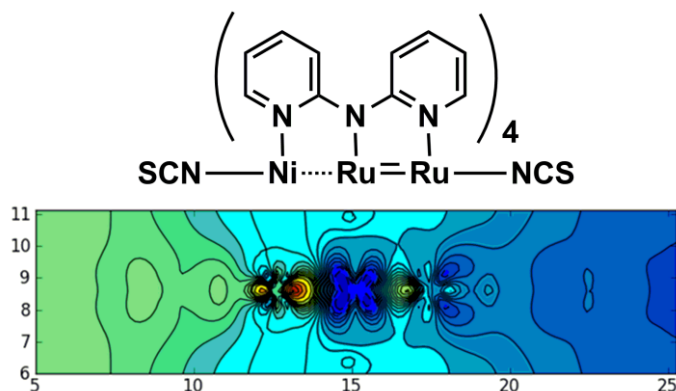
# In Search of Structure-activity Relationships in Paramagnetic Molecular Wires

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Much of the recent momentum in the field of molecular electronics has been centred on organic components, where the conjugated  $\pi$  systems typically provide the dominant transport pathways.[1] Transition metal based systems, in contrast, have been somewhat overlooked despite the fact that their innately flexible electronic structure offers enormous potential. Ligand field effects, changes in redox and spin state and metal-metal bonding all play a critical role in determining the nature of the transport channels near the Fermi level in a putative molecular electronic device. Structure-function relationships – principles that can guide synthetic effort towards target molecules – are not as well developed in the context of transition metal electronics as they are in the organic field. It is clear that asymmetry, either in the molecule or in its contacts to the electrodes, precludes the possibility that current flow is rigorously symmetric, but to what extent does the compositional asymmetry actually perturb the transport channels of interest? Subtle changes in the left-right delocalization of a channel can be controlled through spin polarization, and this can in turn influence rectification ratios. In this presentation I will review recent computational work that seeks to provide a set of guidelines for structure-activity relationships in metal atom chains.



**Figure.** Potential drop across a trimetallic wire.

- [1] Aviram A. and Ratner M. A., "Molecular Rectifiers", *Chem. Phys. Lett.*, **1974**, 29, 277-283.



# ESEEM spectroscopy: Basic theory and application examples

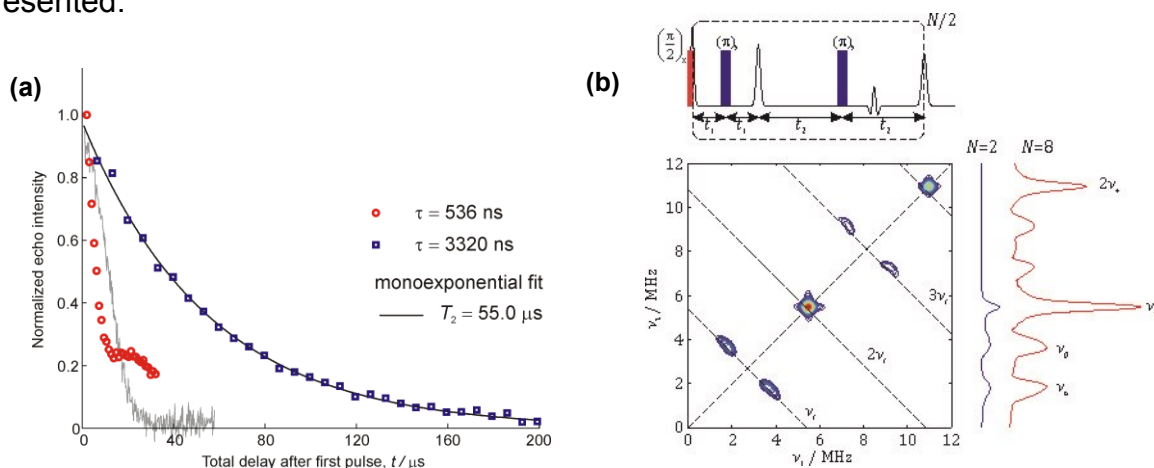
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The electron spin echo envelope modulation (ESEEM) effect is the key element of many powerful pulsed electron paramagnetic resonance (EPR) techniques that are used to determine weak hyperfine and nuclear quadrupole interactions in paramagnetic solids. While the ESEEM phenomenon was originally observed by Mims, Nassau, and McGee back in 1961 and theoretically described later by Mims in 1972, its potential to characterize paramagnetic species has not been fully exploited yet. Current challenges include invention of new methods aimed at resolution and/or sensitivity enhancement, development of fast and efficient simulation programs, and efforts to overcome inherent difficulties appearing in high-spin ( $S > 1/2$ ) systems.

The talk will first give an introduction to ESEEM spectroscopy by presenting the underlying physical effect using both the quantum mechanical and classical description for a model system  $S=1/2$ ,  $I=1/2$ . The most widely used methods based on ESEEM will be briefly discussed with application examples from chemistry, physics, and materials science. We will then demonstrate the pros and cons of this effect in the unconventional field of spin-based quantum computing by discussing two examples in detail: first, the fast manipulation of nuclear spins in hybrid electron-nuclear spin systems, and second, the decoherence mechanisms of atomic hydrogen. Finally, a new ESEEM method [1] inspired by the latter example will be presented.



**Figure.** (a) Decay of electron spin coherence in atomic hydrogen. (b) New ESEEM method

[1] G. Mitrikas, G. Prokopiou, *J. Magn. Reson.*, **2015**, 254, 75-85

## **Synthesis and Characterization of a Variety of Manganese-Zirconium Clusters**

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Heterometallic cluster chemistry is of considerable interest because of the ability of these materials to amalgamate the properties of two different metals. For example, mixed 3d/4f clusters can possess properties enhanced by the combined magnetic properties of each metal type. Heterometallic compounds can also exhibit unique behavior that neither of the two metals display individually (e.g. CTIST and LIESST effects in cyanide-bridged systems). Our group has thus long been exploring the synthesis and characterization of a number of mixed-metal clusters, as have many other groups around the world. Until now, however, there has been very little in the literature involving the exploration of the realm of mixed manganese-zirconium cluster chemistry, and the few available examples have required inert atmosphere conditions and/or multiple steps. We have thus endeavored to perfect synthetic methods to such molecular clusters under aerobic conditions and using commercially available starting materials in order to facilitate the study of this cluster type. We herein present the syntheses and physical properties of three new Mn/Zr clusters, which are all made by a solution method at elevated temperature.

## Women in Physical Sciences – What's the Problem?

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There has been considerable interest in the difficulties facing women in academic roles within the Science Technology Engineering and Mathematics (STEM) subjects. I will specifically consider women working in physical sciences. Initially, an assessment will be made of the situation in this area when compared to other STEM departments, other unrelated subjects and in fact the employment of women in senior industry and business roles as a whole.

Having established that there is significant scope for improvement, the nature of the difficulties will be discussed. There are a number of high profile university-based initiatives being undertaken in the UK, USA and Europe aimed at addressing the issues facing women in STEM subjects. Examples of these will be discussed, the scope of the initiatives will be outlined and evidence of their impact reviewed.

The hypothesis has been made that not enough female students are selecting physical sciences as their career of choice at a young age, even though they may go on to take undergraduate and postgraduate courses in the subjects. There is considerable scope to address this issue and illustrations will be given of how this can be achieved. I will outline the Kendrick School (UK) STEM program and demonstrate what it is doing to promote physical sciences, prior to students making crucial career and therefore subject choices.



Workshop at Kendrick School, Research Council UK- Schools' University Partnership with Imperial College

# A Discovery of a Novel Form of Crystalline Order Suitable for Thermoelectric Applications

Socrates T. Pantelides<sup>1,2,3</sup>

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A new form of crystalline order has been discovered in hexagonal  $\text{CuInS}_2$  nanoparticles and is likely to be present in a large class of ternary tetrahedrally-bonded materials. The cation sublattice is shared by two elements. There exist several ordered structures in which every sulfur has two Cu and two In neighbors, satisfying the “octet rule” that lowers the system’s energy. Theoretical calculations find that these ordered structures have essentially the same energy. The resulting structure, shown in Fig. 1, obtained by aberration-corrected scanning transmission electron microscopy, comprises interlaced domains. The boundaries can be drawn in more than one way as the underlying Bravais lattice is in fact intact. Phase and domain boundaries cost no energy and entail no defects or strain.

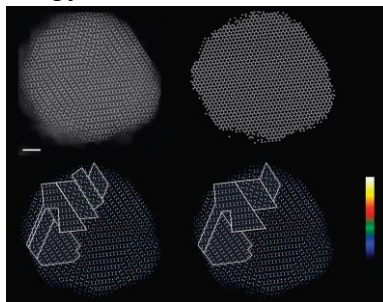


Fig. 1 Top left: Z-contrast image of a  $\text{CuInS}_2$  nanoparticle (S atoms are not visible). Top right: Same image with all Cu and In atoms shown identical. Bottom: Two different sets of boundaries.

Electronic transport is not impeded by the boundaries because the pseudopotentials of Cu and In are similar, but heat transport by phonons is sensitive to the mass discontinuities at boundaries. This features plus the ultrasmall domain size, make interlaced crystals unique for thermoelectric applications that require high electrical and poor thermal conductivities. Calculations will be presented demonstrating that the thermoelectric coefficient is indeed strongly enhanced by interlacing.

[1] X. Shen et al. *Nature Commun.* 2014, **5**, 543.

# Visualization of Charge Carrier Dynamics in Nanowires with Pump-Probe Microscopy

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A detailed understanding of the factors that govern the motion of mobile charge carriers through nanostructures is critical to many emerging nanotechnologies in electronics, optoelectronics and solar energy conversion. While the motion of charge carriers at low carrier densities is uncorrelated and easy to understand, many active electronic components operate at high carrier concentrations resulting from heavy doping or high injection. In this regime, carrier-carrier interactions and other many body effects (e.g. dopant/carrier interactions, electron screening, and electron-hole scattering) must be considered. We have combined ultrafast pump-probe spectroscopy with optical microscopy [1, 2] to directly image the charge carrier dynamics in individual Si nanowires (NWs) with both spatial and temporal resolution.

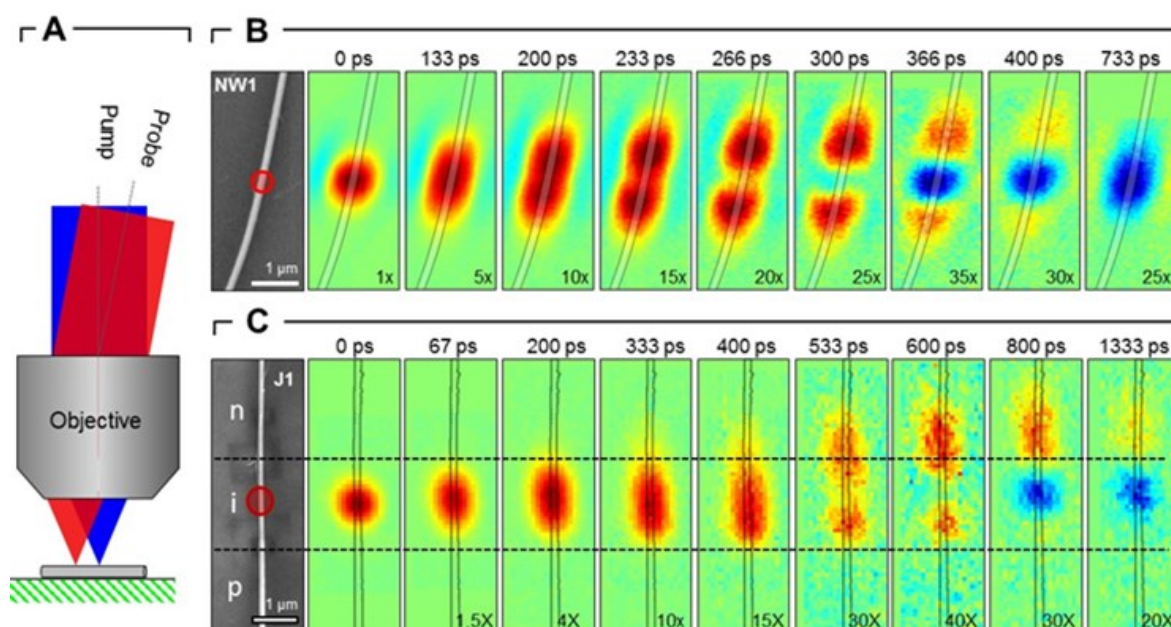


Figure: Pump-probe microscopy images showing charge carrier motion in undoped Si nanowires and a nanowire p-type/intrinsic/n-type junction.

1. Gabriel, M. M. et al. "Direct Imaging of Free Carrier and Trap Carrier Motion in Silicon Nanowires by Spatially-Separated Femtosecond Pump-Probe Microscopy", *Nano Lett.* 2013, 13, 1336-1340.
2. Gabriel, M. M. et al. "Imaging Charge Separation and Carrier Recombination in Nanowire p-i-n Junctions Using Ultrafast Microscopy", *Nano Lett.* 2014, 14, 3079-3087.

# New Structural Types from the Use of Polyol Type Ligands in Mn, Mn/Ni and Mn/Ln Cluster Chemistry

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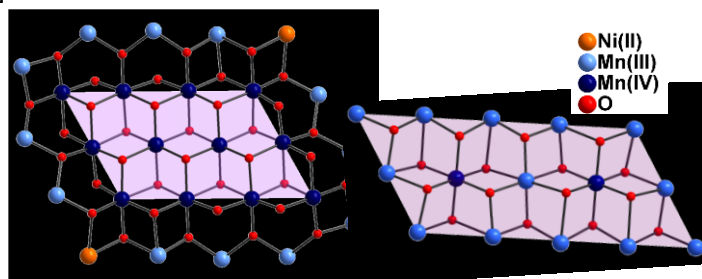
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One successful synthetic approach towards new high nuclearity compounds involves the use of chelates containing alcohol groups, since alkoxides are good bridging groups and favour the formation of polynuclear products.[1] In this context, we have been investigating a variety of diols and aminoalcohols in Mn and Fe carboxylate chemistry and isolated several polynuclear compounds with uncommon structural features and interesting magnetic properties.[2] We recently expanded this investigation to include ligands with more ROH groups in order to study the effect of higher linking ability on the nuclearity and the magnetic properties of the resulting products. Herein, we will describe the initial results of these investigations,[3] which include amongst others,  $Mn_4Ln_2$ ,  $Mn_{15}$  and  $Mn_{24}Ni_2$  clusters, the latter consisting of discrete  $[3 \times 5]$  and encapsulated into a  $Mn^{III}_{12}Ni_2$  loop  $[3 \times 4]$  grid – like aggregates.  $Mn_{24}Ni_2$  is among the highest nuclearity heterometallic  $Mn_xM_y$  clusters reported to date (Figure). [4]



**Figure.**Representations of the structural cores of the clusters  $Mn_{24}Ni_2$  (left) and  $Mn_{15}$  (right) that will be presented in this work.

[1] A. J. Tasiopoulos, S. P. Perlepes, *Dalton Trans.*, **2008**, 5537.

[2] (a) M. Charalambous, E. E. Moushi, C. Papatriantafyllopoulou, W. Wernsdorfer, V. Nastopoulos, G. Christou and A. J. Tasiopoulos, *Chem. Commun.*, **2012**, 5410; (b) C. Papatriantafyllopoulou, C. M. Kizas, M. J. Manos, A. Boudalis, Y. Sanakis, A. J. Tasiopoulos, *Polyhedron*, **2013**, *64*, 218.

[3] S. Zartilas, C. Papatriantafyllopoulou, T. C. Stamatatos, V. Nastopoulos, E. Cremades, E. Ruiz, G. Christou, C. Lampropoulos, A. J. Tasiopoulos, *Inorg. Chem.*, **2013**, *52*, 12070.

[4] M. Charalambous, S. Zartilas, E. E. Moushi, C. Papatriantafyllopoulou, M. Manos, T. Stamatatos, S. Mukherjee, V. Nastopoulos, G. Christou, A. J. Tasiopoulos, *Chem. Commun.*, **2014**, 9090.

**Acknowledgments:** This work was supported by University of Cyprus (internal research grant). We also thank the European Union Seventh Framework Program (FP7/2007-2013) under Grant agreement numbers: PCIG09-GA-2011-293814) and PIRSES-GA-2011-295190.



# Synthesis and Properties of Polydicyclopentadiene Gels

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The ring opening metathesis polymerization (ROMP) reaction yields polymeric materials with unique mechanical, optical, electrical and chemical properties, and has been adopted recently for the synthesis of robust organic aerogels [1]. ROMP can be catalyzed by a broad range of metal-based catalytic systems, with forerunners those of ruthenium, molybdenum and tungsten [2]. Bimetallic complexes with metal-metal bonds have been scarcely employed, although they provide more precise control over stereoselectivity, because both metal centers can be involved in the reaction. Among those,  $\text{Na}[\text{W}_2(\mu\text{-Cl})_3\text{Cl}_4(\text{THF})_2]\cdot(\text{THF})_3$  turns out an efficient and inexpensive initiator for ROMP of a range of cycloolefins [3]. In this study, we implement this catalyst for the synthesis of polydicyclopentadiene (PDCPD) gels and we compare their morphostructural characteristics and properties to those of PDCPD gels obtained with conventional catalysts.

[1] S. H. Kim, M. A. Worsley, C. A. Valdez, S. J. Shin, C. Dawedeit, T. Braun, T. F. Baumann, S. A. Letts, S. O. Kucheyev, K. J. J. Wu, J. Biener, J. H. Satcher Jr., A. V. Hamza, *RSC Advances*, **2012**, 2, 8672; D. P. Mohite, S. Mahadik-Khanolkar, H. Luo, H. Lu, C. Sotiriou-Leventis, N. Leventis *Soft Matter*, **2013**, 9, 1516; *Soft Matter*, **2013**, 9, 1531.

[2] [http://www.nobelprize.org/nobel\\_prizes/chemistry/laureates/2005/grubbs-lecture.html](http://www.nobelprize.org/nobel_prizes/chemistry/laureates/2005/grubbs-lecture.html); [http://www.nobelprize.org/nobel\\_prizes/chemistry/laureates/2005/schrock-lecture.html](http://www.nobelprize.org/nobel_prizes/chemistry/laureates/2005/schrock-lecture.html).

3. G. Floros, N. Saragas, P. Paraskevopoulou, N. Psaroudakis, S. Koinis, M. Pitsikalis, N. Hadjichristidis, K. Mertis, *Polymers*, **2012**, 4, 1657.

This research has been co-financed by the European Union (European Social Fund – ESF) and Greek national funds through the Operational Program "Education and Lifelong Learning" of the National Strategic Reference Framework (NSRF) – Research Funding Program: THALES. Investing in knowledge society through the European Social Fund. MIS: 377252.



# Tuning Strategies for Cluster-Based Water Oxidation and Reduction Catalysts

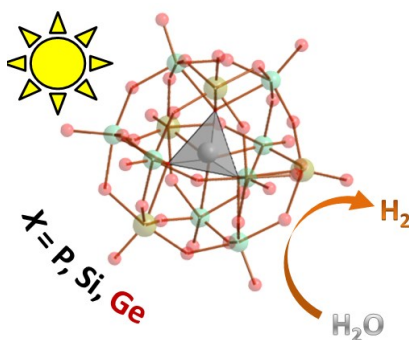
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Artificial photosynthesis as an elegant pathway to clean and sustainable solar fuels is in the focus of current worldwide research interest. Molecular systems provide excellent opportunities to study structure-activity relationships for efficient and economic catalyst design.

Inspired by the  $\{\text{CaMn}_4\text{O}_5\}$  OEC of photosystem II, we have brought forward the cubane-type water oxidation catalyst (WOC)  $[\text{Co}^{\text{II}}_4(\text{hmp})_4(\mu\text{-OAc})_2(\mu_2\text{-OAc})_2(\text{H}_2\text{O})_2]$  as a model system for studying the influence of transition metal nuclearity and ligand environment on the WOC performance.[1] Mechanistic and X-ray absorption spectroscopy investigations outline the stability of the  $\{\text{Co}(\text{II})_4\text{O}_4\}$  core in solution together with flexible exchange behavior of the aqua and monodentate acetate ligand architecture. Flash photolysis and modeling studies shed new light on the crucial influence of different buffer media on the catalytic activity.



**Figure 1.** Photocatalytic water reduction with  $[\text{Ni}(\text{H}_2\text{O})\text{XW}_{11}\text{O}_{39}]^{n-}$  ( $\text{X} = \text{P}, \text{Si}, \text{Ge}$ ) POMs.

In contrast to cubane WOCs, polyoxometalate WOCs (POMs) feature a fascinating interplay of structural diversity vs. complex structure-activity relationships. Most recently, POMs have also been explored as water reduction catalysts (WRCs). We have systematically investigated the influence of the heteroatom on the WRC activity among the  $[\text{Ni}(\text{H}_2\text{O})\text{XW}_{11}\text{O}_{39}]^{n-}$  ( $\text{X} = \text{P}, \text{Si}, \text{Ge}$ ) series (Figure 1).[2] The comparison of photo- and electrocatalytic results illustrates the diverse reaction pathways of POM-WRCs.

[1] F. Evangelisti, R. Güttinger, R. Moré, S. Luber, G. R. Patzke, *J. Am. Chem. Soc.* **2014**, 135, 18734.

[2] K. von Allmen, R. Moré, R. Müller, J. Soriano-López, A. Linden, G. R. Patzke, *ChemPlusChem*, in print.



# Metal-Assisted Ligand Transformations, Chemical Reactivity and Magnetism in Nickel Oximate Clusters

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The *a*-benzoin oxime (aboH<sub>2</sub>) belongs in the hydroxy oximes group and its coordination chemistry still remains almost unexplored. Only a few *a*-benzoin oxime complexes have been isolated and structurally characterized, some of which from our research group, which were found to adopt the structure of a “wheel”. Attempting to further develop the coordination chemistry of aboH<sub>2</sub> we studied the reaction system Ni(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O / aboH<sub>2</sub> / base, from which we isolated and structurally characterized a family of octanuclear Ni(II) cage templated by a rare  $\eta^3:\eta^3:\mu_6\text{-O}_2^{2-}$  produced by the dioxygen activation, where the reducing agent for the O<sub>2</sub> reduction appears to be the ligand (aboH<sub>2</sub>) used in the reaction mixtures, which was found within the nickel cages in its oxidized form.[1] Despite the presence of the peroxide within the core of the cages, they are exceptionally thermally stable and can undergo reactivity reactions under reflux. The [Ni<sub>8</sub>] core is maintained during the reactivity experiments while selective ligand substitution and ligand rearrangement were observed. These structural alterations resulted in a dramatic change of the magnetic properties of the clusters.

[1] Perivolaris, A.; Stoumpos, C. C.; Karpinska, J.; Ryder, A. G.; Frost, G. M.; Mason, K.; Prescimone, A.; Slawin, A. M. Z.; Kessler, V. G.; Mathieson, J. S.; Cronin, L.; Brechin, E. K.; Papaefstathiou, G. S. *Inorg. Chem. Front.*, **2014**, 1, 487.

**Acknowledgments:** This research has been co-financed by the European Union (European Social Fund – ESF) and Greek national funds through the Operational Program "Education and Lifelong Learning" of the National Strategic Reference Framework (NSRF) - Research Funding Program: THALES. Investing in knowledge society through the European Social Fund.

## **Paramagnetic Nanomaterials for Optical Biological Imaging: MOFs Incorporating Lanthanide Cations Emitting in the Near-Infrared**

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Fluorescence and luminescence are detection techniques that possess important advantages for bioanalytical applications and biological imaging: high sensitivity, versatility and low costs of instrumentation.

The luminescence of lanthanide cations has several complementary advantages over the fluorescence of organic fluorophores and semiconductor nanocrystals, such as sharp emission bands for spectral discrimination from background emission, long luminescence lifetimes for temporal discrimination and strong resistance to photobleaching. In addition, several lanthanides emit near-infrared (NIR) photons that can cross important depths of tissues for non-invasive investigations and that results in improved detection sensitivity due to the absence of native NIR luminescence from tissues and cells (autofluorescence). The main requirement to generate lanthanide emission is to sensitize them with an appropriate chromophore ("antenna effect").

An innovative concept for such sensitization of NIR-emitting lanthanides is proposed herein: the current limitation of low quantum yields experienced by most mononuclear lanthanide complexes is compensated by using a large number of lanthanide cations and by maximizing the absorption of each discrete molecule, thereby increasing the number of emitted photons per unit of volume and the overall sensitivity of the measurement. To apply this concept, we have created several types of MOFs and dendrimer macromolecular complexes and succeeded in generating highly emissive NIR MOFs. We will discuss their designs, synthesis, structures, photophysical properties and their applications for biological imaging of living cells with NIR microscopy.

[1] Foucault-Collet, A., Gogick, K. A., White, K. A., Villette, S., Pallier, A., Collet, G., Kieda, C., Li, T., Geib, S. J., Rosi, N. L., & Petoud, S. *PNAS*, **2013**, *110*, 17199 – 17204.

# **Vortex Matter Properties of $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ Superconductor Probed by ac Susceptibility Measurements**

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The vortex matter (Abrikosov state) in type II superconductors, under the influence of weak pinning centers constitutes an interesting physical system having many similarities with conventional matter. Despite the intensive research effort having been devoted, in studying the vortex matter, the discovery of new superconductors still keeps many surprises and not well understood novel physical effects. By employing ac-susceptibility and specific heat measurements, the vortex matter properties of a  $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$  single crystal, as a function of temperature for constant external magnetic field and of the magnetic dc-field for constant temperature, were studied. The frequency dependence of the ac-susceptibility for temperatures and selected applied field are also presented. The irreversibility lines ( $H_{\text{irr}}(T, \Theta)$ ) were estimated from the onsets of the third harmonic susceptibility amplitude and can be reproduced from the equation,  $H_{\text{irr}} = H_{0,\Theta}(1-T/T_c)^n$ , within  $\sim 1$ . The  $H_{c2}$ -line is deduced from specific heat measurements, located above the irreversibility line. The isofield measurements of the real part of the fundamental ac-susceptibility  $\chi'(T)$  revealed a narrow diamagnetic deep which corresponds to a local peak in the screen electrical currents. The overall behavior resembles the peak effect, observed in all type II superconductors with weak disorder. The second peak line is located below and near  $H_{\text{irr}}$ -line. The peak effect is disappeared for  $\mu_0 H < 0.2$  Tesla and it transformed to a sudden drop of the critical electrical current. Using the results of the collective pinning theory and Liedmann type criteria, the vortex matter phase diagram was reproduced, by adopting a  $\delta T_c$ - pinning mechanism, a Ginzburg number  $Gi \approx 7 \times 10^{-4}$  and a zero temperature Larkin parameter  $D_0 \approx 0.21$ .

# Flexibility of Ligands as a Source of Structural Pluralism in Coordination Polymer Chemistry

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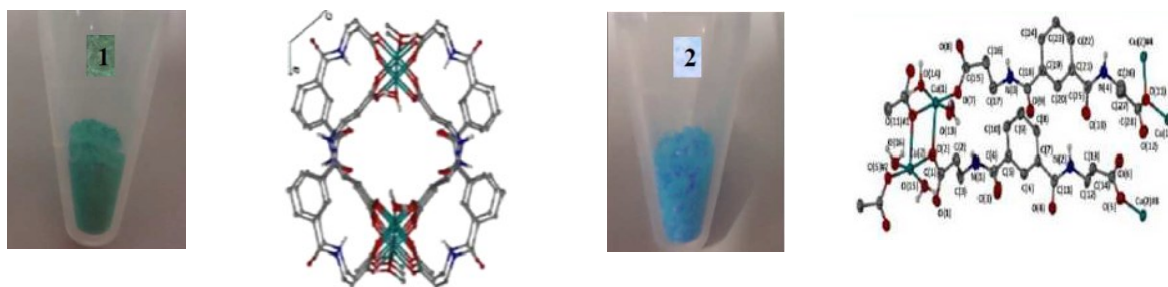
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Over the last 25 years there has been an explosion in publications in the field of coordination polymers (CPs) and/or metal-organic polymers (MOFs).<sup>1</sup> Gradually the conditions for the design and construction of those materials have been created leading to the development of isorecticular chemistry.<sup>2</sup> Eventually, a third generation of materials has emerged, which are flexible MOFs, named soft porous crystals (SPCs).<sup>3</sup>

Despite the success in the design of MOFs utilizing rigid ligands, the use of flexible ligands, especially in cases where groups that allow additional weak interactions (such as H-bonds) are present, leads to the formation of unprecedented structures, with, sometimes, interesting properties.

In this work, we present a series of results coming from our attempts to use flexible ligands for the formation of coordination polymers. We used three different ligand categories, a) polycarboxylic acids based on aliphatic carbon chains, β) pseudopeptides, and γ) aminocarboxylic acids, while the metal ions belong to transition metals and rare earths.

Some properties of the prepared coordination polymers, such as reversible loss of solvated molecules, heterogeneous catalysis and ion exchange, are also described.



**Figure.** Two products derived by the reaction of copper(II) salts with isophthaloylbis-β-alanine. 1:  $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ , 2:  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$

<sup>1</sup> G. Férey, *Struct. Bond.*, 2009, **132**, 87.

<sup>2</sup> D. J. Tranchemontagne, J. L. Mendoza-Cortes, M. O’Keeffe, and O. M. Yaghi, *Chem. Soc. Rev.*, 2009, **38**, 1257.

<sup>3</sup> A. Schneemann, V. Bon, I. Schwedler, I. Senkovska, S. Kaskel, R. A. Fischer, *Chem. Soc. Rev.*, 2014, **43**, 6062.

# Nickel(II) /Lanthanide(III) Complexes: Synthetic, Structural and Magnetic Studies

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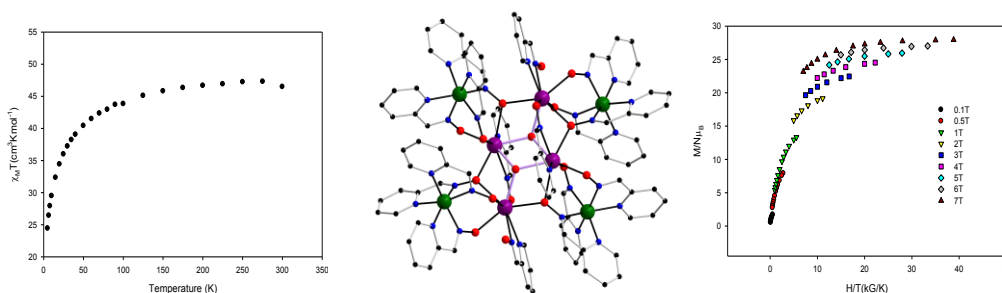
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Nickel(II) /lanthanide(III) complexes are of great importance in the field of 3d/4f-metal chemistry and thus in Single Molecule Magnetism [1-3]. The significant spin of  $\text{Ln}^{\text{III}}$  ions, as well as the magnetic anisotropy which both metal ions may exhibit lead to interesting Single Molecule Magnets (SMMs). We shall present our synthetic efforts to combine  $\text{Ni}^{\text{II}}$  and  $\text{Ln}^{\text{III}}$  ions in complexes with 2-pyridyl oximes as ligands. Structural, spectroscopic and magnetic studies will be described for families of  $\text{Ni}^{\text{II}}\text{Ln}^{\text{III}}$ ,  $\text{Ni}_4^{\text{II}}\text{Ln}_4^{\text{III}}$  and  $\text{Ni}_8^{\text{II}}\text{Ln}_8^{\text{III}}$  complexes.



- [1] C. Papatriantafyllopoulou, Th. C. Stamatatos, C. G. Efthymiou, L. C. Silva, F. A. Almeida Paz, S. P. Perlepes and G. Christou, *Inorg. Chem.* **2010**, *49*, 9743.
- [2] V. Chandrasekhar, P. Bag, W. Kroener, K. Gieb and P. Müller, *Inorg. Chem.* **2013**, *52*, 13078.
- [3] C. D. Polyzou, C. G. Efthymiou, A. Escuer, L. C. Silva, C. Papatriantafyllopoulou and S. P. Perlepes, *Pure Appl. Chem.* **2013**, *85*, 315.

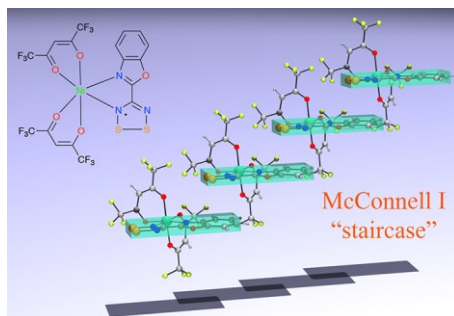
# Magnetic Properties of Metal-Radical Complexes using Thiazyl Ligands

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The so-called “metal-radical approach” to designing molecule-based magnetic materials takes advantage of strong exchange coupling between the moments of a paramagnetic metal ion and the paramagnetic ligand to which it is coordinated. Typically, the nature of the exchange coupling can be understood and predicted based on a simple orbital-overlap model. Employing paramagnetic ligands to mediate strong and predictable magnetic coupling between metal ion moments is an attractive model for material design. We are interested in extending the metal-radical approach by creating paramagnetic ligands that will also engage in *intermolecular* interactions, through so-called “pancake bonding”, highly directional electrostatic contacts, or weaker van der Waals contacts. Our current work on developing paramagnetic ligands designed using cyclic thiazyl “building blocks” will be presented. This work includes examples of molecule-based materials that exhibit ferromagnetic (FM) ordering, antiferromagnetic (AF) ordering, and reentrant phase transitions, arising from the design principles described above.



**Figure 1.** Intermolecular FM exchange coupling between Ni(II)-radical complexes is best understood in the context of the McConnell I mechanism.[1]

[1] E. M. Fatila, R. Clérac, M. Jennings, K. E. Preuss\*, *Chem. Commun.*, **2013**, 49, 9431-9433.

# Geometric Factors in the Magnetoresistance of InAs

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In this talk, I will describe the magnetoresistance (MR) effect in n-doped InAs and InAs/metal hybrid devices with geometries tailored to elucidate the physical mechanism and the role of geometry in the MR. Despite the isotropic Fermi surface in InAs, we observe a strong intrinsic MR in the InAs epilayer due to the existence of a surface conducting layer. Experimental comparison confirms that the extraordinary MR in the InAs/metal hybrids outperforms the orbital MR in the Corbino disk in terms of both the MR ratio and the magnetic field resolution. The results also indicate the advantage of a two-contact configuration in the hybrid devices over a four-contact one with respect to the magnetic field resolution. This is in contrast to previously reported results, where performance was evaluated in terms of the MR ratio and a four-contact configuration was found to be optimal. By applying Kohler's rule, we find that at temperatures above 75 K the extraordinary MR violates Kohler's rule, due to multiple relaxation rates, whereas the orbital MR obeys it. This finding can be used to distinguish transport in inhomogeneous medium from homogeneous medium.

[1] "Geometric factors in the magnetoresistance of n-doped InAs epilayers", Jian Sun, Yeong-Ah Soh, and Jurgen Kosel, J. Appl.Phys. 114, 203908 (2013).

# Naphthalene-based Diols as Bridging Ligands in Polynuclear Metal Cluster Chemistry: Synthesis, Structures and Magnetic Properties

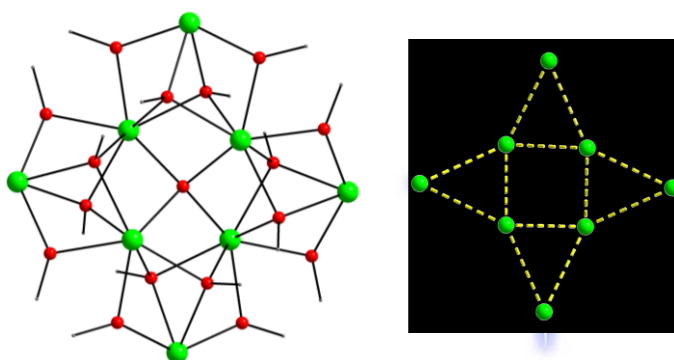
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The synthesis of new polynuclear molecular compounds (clusters) that contain paramagnetic metal centers continues to attract the interest of many research groups. Reasons for such an interest are numerous and include the architectural beauty of these species, as revealed by their structural determination, and their applications in various fields of applied science such as magnetism, optics and catalysis. The crystal field environment and consequently the organic and inorganic bridging ligands bound to the metal ions constitute some of the most crucial factors for increasing the nuclearity of a cluster compound and affecting their electronic properties. We have recently started a program aiming at the exploration of the coordination chemistry of bulky naphthalene-based diols with transition metal ions and/or lanthanides as a means of obtaining clusters with new structural motifs and interesting magnetic properties, such as single-molecule magnets and molecular magnetic refrigerants [1]. In this presentation we will discuss the synthesis, structural and magnetic properties of series of 3d/4f- and 4f-metal clusters.



**Figure 1.** The core of a  $\text{Ln}_8$  cluster (left) and its “Christmas-star”-like topology (right).

[1] D. I. Alexandropoulos et al., *Inorg. Chem.*, **2014**, 53, 5420



## Metal-Organic Frameworks for Sensing Applications

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In recent years, there has been an increasing interest in metal–organic frameworks (MOFs) for the versatile architectures and intriguing topologies as well as for their wide potential applications. Generally, the structural and functional features of such materials greatly depends on the selection of the organic ligands and metal ions, as well as on the reaction pathways. In general the synthesis of MOFs is achieved under mild conditions (e.g. solution chemistry, solvothermal synthesis) and most of the times is high yielding and scalable, features that make MOFs attractive targets for technological applications. MOFs have advanced the last 20 years due to their inherent ability to host molecules within their nanosized pores. Due to the host-guest interactions some of the host's properties change and that makes them perfect candidates for sensing technologies.

Herein we will present our efforts to synthesize and characterize oxalamide based MOFs for sensing volatile organic compounds originating from food (fish) spoilage. These thermally stable MOFs are capable of altering their fluorescence intensity upon capture of the targeted analytes.

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# Synthesis and Characterization of New Homo- and Heterometallic Manganese Clusters

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3d homo- and heterometallic clusters are of great interest to many research groups, including ours, due to their often fascinating structures and interesting physical properties, particularly those of relevance to the field of molecular magnetism. Such clusters bring to materials nanoscience the advantages afforded by molecular chemistry, such as room temperature synthesis in solution, crystallinity, monodispersity, and facile modification of the ligation sphere. Manganese is one of the 3d metals of choice for such studies, being stable in multiple oxidation states and having shown a great propensity to yield a variety of cluster types, as well as displaying significant magnetoanisotropy arising from the Jahn-Teller distortion of octahedral Mn<sup>III</sup>. As a result, Mn/O cluster chemistry often leads to compounds with interesting structural, magnetic, and other physical properties. The inclusion of alkaline earth, main group or lanthanide metal ions in Mn chemistry has often yielded interesting structural topologies not accessible in homometallic Mn clusters due to the high coordination number of the heterometal. Such clusters have also proven of relevance to a wide variety of areas, including single-molecule magnets and bulk mixed-metal oxide systems, where the unusual structural types and/or properties can be attributed to the influence of the heterometal. Herein, the syntheses, structural characterization, and physical properties of some new homo- and heterometallic Mn clusters will be presented.

# Cationic Group 13 Compounds: Very Strong Lewis Acids and Some Surprisingly Weak Ones

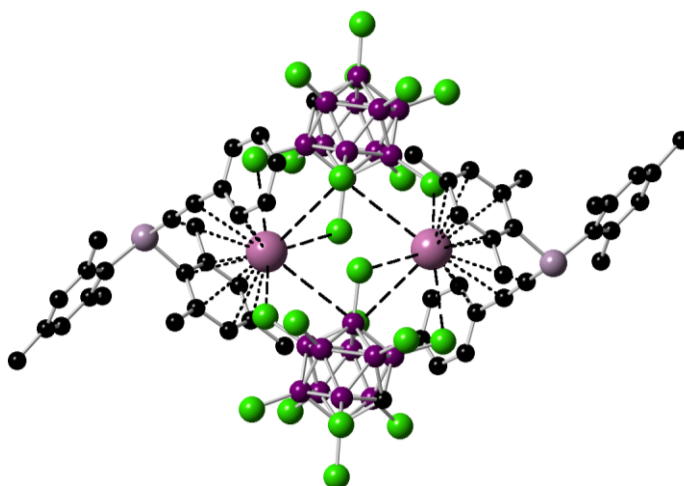
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Alkide abstraction from organoaluminum and –gallium precursors leads to the ionic or ion-like species  $[R_2M]^+[WCA]^-$  (WCA = weakly coordinating anion such as  $[CHB_{11}Cl_{11}]^-$ ). These compounds are very strong Lewis acids, whose metal centers are stabilized in the solid state either by contacts to the anion or by intramolecular  $M\cdots C$  contacts with the  $\pi$ -system of the substituents. They can be applied as catalysts for intramolecular hydroamination of aminoalkenes and hydrosilation of olefins and carbonyl functional groups including  $CO_2$ . [1] Depending on the Lewis acid and solvent applied, the products of the  $CO_2$  reduction are  $CH_4$ , toluene or methoxysilanes.

The redox reaction of  $Ag[CHB_{11}Cl_{11}]$  with indium or gallium metal affords the arene solvated ionic species  $[M(arene)_n][CHB_{11}Cl_{11}]$ , which contain indium or gallium in the less common +1 oxidation state. Due to their low oxidation state their Lewis acidity is rather low. For example, interactions with phosphines are very weak based on  $^{31}P$  NMR spectroscopic data. Furthermore, a diarylphosphinoalkyne coordinates to the indium cation through the triple bond, an aromatic ring and several long  $In\cdots Cl$  contacts with the anion but not through a phosphorus donor center.



**Figure 1.** Structure of  $[(Mes_2PC\equiv CPh)In][CHB_{11}Cl_{11}]$ .

[1] R.J. Wehmschulte, M. Saleh, D.R. Powell, *Organometallics*, **2013**, 32, 6812-6819.

## Coordination Chemistry with Organic $\pi$ -Radicals: Where are the Electrons?

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In recent years it has become clear that the tridentate N-heterocyclic ligand 2,2':6',2''-terpyridine (tpy) can exist in-at least-three(!) distinctly different oxidation levels in octahedral transition metal ion complexes. Homolepticbis(terpyridine) metal complexes  $[M(tpy)_2]^m$  often form electron transfer series where m ranges from 4+ to 3-. What are the electronic structures of such species containing neutral ( $tpy^0$ ), monoanionic $\pi$ -radicals ( $tpy^{\bullet-}$ )<sup>1-</sup> or dianions ( $tpy^{2-}$ )<sup>2-</sup> (with  $S = 0$  or 1). How can we safely elucidate these oxidation levels in a given compound? Upon stepwise reductions of  $[M(tpy)_2]^{3+}$  when are the metal ions and when are the ligands reduced? The compounds serve as electron reservoirs and have important implications for their reactivity (catalysis).

# Thermally and Photochemically Activated Diradicals: From Small Molecule Bioreagents to Nanomedicine Applications for Biopolymers

Jeffrey M. Zaleski

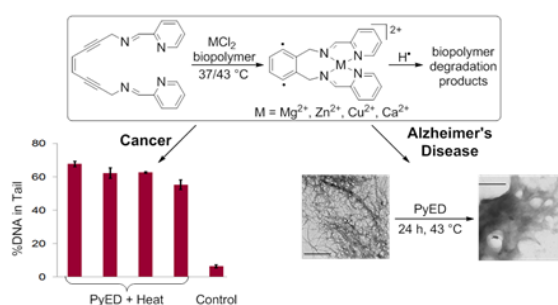
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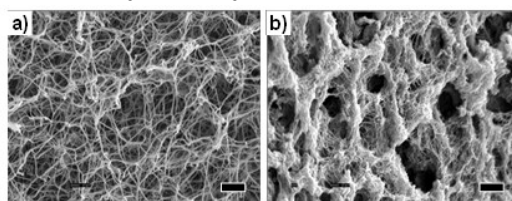
Our research interests lie in developing thermal and photochemical-Bergman cyclization reactivity in inorganic small molecules, porphyrins, and nanoparticle surfaces for carbon-based polymerization reactions, or as nature has taught us, biologically-relevant H-atom abstraction reactivity. While a considerable amount of our efforts are devoted to developing fundamental metal-catalyzed cyclization reactions, we have also applied these motifs to a subset of natural biopolymers such as  $\beta$ -amyloid plaques and fibrin clots.

Disease states resulting from metal-mediated biopolymer deposition can arise when the natural cleavage mechanisms become inoperative or function poorly, such as the formation of  $\beta$ -amyloid plaques which have been connected to the neurodegenerative disease Alzheimer's, as well as thrombotic disease (atherosclerosis) leading to heart attack or stroke. Current treatment options for  $\beta$ -amyloid plaque buildup involve inhibition or activation of specific enzymes involved in the disease pathway, while acute arterial thrombosis is combated via the use of anti-platelet agents or anti-coagulants that inhibit the thrombus. In the latter case, side effects associated with such anti-coagulants involve the risk of systemic bleeding which can supersede the benefit of the antithrombotic therapy.

Our approach to these problems involves developing small molecule enediyne ligands that extract metal directly from the plaque (Cu, Zn, or Ca), or incorporation of diradicals-generating ligands into optically-active Au and magnetically responsive  $\text{Fe}_3\text{O}_4$  nanoarchitectures. Small molecules with  $\text{N}_4$ -coordination have been developed for disaggregation of  $\beta$ -amyloid plaques by *in situ* activation and radical-formation upon chelation of Zn(II) and Cu(II), while larger-payload particles that can be activated photo-thermally or by magnetic induction hyperthermia are applied to dissolve fibrin clots. This presentation will describe several chemical and applied aspects of this work.



**Figure 1.** Dissolution of biopolymers by metal chelation-induced radical formation.



**Figure 2.** SEM images showing the fibrin clot surface morphology change upon photolysis. A) initial, b) after irradiation at  $\lambda = 514 \text{ nm}$ , 100 mW for 4 h. Scale = 2  $\mu\text{m}$ .

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