

Preface

Hideki Hashimoto (Project Leader)

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Shortage of energy and water resources (= food production) and the global warming are the grave crises that the human beings on this planet are currently facing. These crises are generated during the course of the development of cities. And now they are seriously affect the life of the people, who are living in the modern cities. In this sense, the global crises can be regarded as a symbolic matter of civic problems. They cannot be simply ignored by us, who are living in one of the major ordinance-designed cities “Osaka”. Therefore it is a challenging subject to find out possible ways to suggest powerful measures to cope well with these problems.

There are three scientific faculties (Faculties of Science, Engineering, and Human Life Science) at the Sugimoto campus in Osaka City University. These faculties are accounted to be the treasure troves of Osaka city in the scientific field. Since the issue of global crisis extends over the whole planet, it is required to assimilate the knowledge accumulated by the scientists in these three independent faculties to correctly deal with the urgent issue of the global crises. This is an exact reason why we have launched a new research institute whose members are carefully selected from the above three faculties. The new research institute is named as “The Integrated Advanced Research Institute of Osaka City University”. The first approved research project in this institute is the one that challenges the regeneration of the urban environment, and it tries to tackle the problems of biological systems and the sound and innovative use and circulation of energy and groundwater. The project is constituted with three strategic research subjects and is guided by three research teams as listed below.

- Subject of Team A: Development and Industrial Application of the Next Generation Energy Resources
- Subject of Team B: Utilization of Groundwater for the Preservation of Civil Environment and for the Prevention against Geo-hazard
- Subject of Team C: Space and Time Evolution of the Environment and Biological Systems in the Urban Area

These subjects cover the broad area of scientific research ranging from microscopic space to macroscopic prediction. In order to effectively use the outcome of the project it is very important to facilitate the mutual communication among the three research groups. Without mutual understandings it is impossible to meet the problems of the urban environment and the global issues. Furthermore, the outcomes of the project should be informed toward all over the world.

This international Symposium is held on the subject of environmental research. Eminent active researchers at home and abroad in the relevant research fields are invited

as keynote speakers of this symposium. I hope that, through an animated discussion, we can share common realization toward the resolution of worldwide affair. Finally, I strongly wish that this symposium becomes small but great first step for the dispatch of intelligence under the slogan of “Saving the World Starting from Osaka”.

Hideki Hashimoto (Project Leader)
CREST-JST and Graduate School of Science, Osaka City University

Invited Speakers

Richard J. Cogdell (University of Glasgow, UK)

Thomas A. Moore (Arizona State University, USA)

Ana L. Moore (Arizona State University, USA)

Bruno Robert (Institute of Biology and Technology of Saclay, FRA)

Leroy Cronin (University of Glasgow, UK)

Timothy J. Storr (Simon Fraser University, CAN)

Lawrence R. Sita (University of Maryland, USA)

L. James Wright (University of Auckland, NZ)

Osamu Ishitani (Tokyo Institute of Technology, JPN)

Tsutomu Miyasaka (Toin University of Yokohama, JPN)

Programme

8th March, 2010

- 13:30~14:00 Opening Remarks
Hideki Hashimoto
Osaka City University (JPN)
- 14:00~15:00 Plenary Lecture
Richard J. Cogdell.....1
University of Glasgow (UK)
“What can we learn from photosynthesis about
how to use solar energy to produce fuels? ”
- 15:00~16:00 **Bruno Robert**.....2
Institute of Biology and Technology of Saclay (FRA)
“Bioenergetic Studies in the Parisian Area”
- 16:00~16:15 Interval
- 16:15~17:15 **Thomas A. Moore**.....3
Arizona State University (USA)
“Combining Technology with Biology
for Efficient Energy Production and Use”
- 17:15~18:15 **Osamu Ishitani**.....4
Tokyo Institute of Technology (JPN)
“Artificial photosynthetic systems
for reduction of NADP model compounds and CO₂”
- 18:15~19:45 Banquet
- 19:45~21:45 Poster Sessions, Mixer

9th March, 2010

09:00~10:00	Timothy J. Storr5 Simon Fraser University (CAN) “Correlation of Electronic Structure and Reactivity - The Case of Oxidized Metal Salens”
10:00~11:00	Tsutomu Miyasaka6 Toin University of Yokohama (JPN) “Photoelectrochemical Simulation of Energy Conversion in the Photosynthetic Primary Processes and Design for Film-type High-efficiency Dye-sensitized Solar Cells”
11:00~11:10	Interval
11:10~12:10	Ana L. Moore7 Arizona State University (USA) “Design of photoelectrochemical cells for the splitting of water and fuel production”
12:10~12:50	Nobuo Kamiya8 Osaka City University (JPN) “Structure around Oxygen-Evolving Mn ₄ O _x Ca-Cluster of Photosystem II Complex from <i>Thermosynechococcus vulcanus</i> ”
12:50~13:50	Lunch
13:50~14:50	Leroy Cronin9 University of Glasgow (UK) “Manganese-Polyoxometalate Architectures: Towards Water Oxidation Catalysts Inspired by Photosystem II”
14:50~15:50	L. James Wright10 University of Auckland (NZ) “Green Oxidation Catalysts”

15:50~16:00	Interval	
16:00~17:00	Lawrence R. Sita	11
	University of Maryland (USA)	
	“New Platforms for Probing Early Transition Metal Trends for Bimetallic Dinitrogen Activation and N≡N Bond Cleavage”	
17:00~17:10	Closing Remarks	

Conference Venue: Awaji Yumebutai International Conference Center

<http://www.yumebutai.org/english/index.html>



What can we learn from photosynthesis about how to use solar energy to produce fuels?

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Currently in the developed world we obtain about 70% of our energy requirements by burning fossil fuels such as oil, coal and gas. Due to the fact that supplies of both oil and gas are fast running out and because of worries about climate change and its links to rises in the concentration of atmospheric carbon dioxide mankind urgently needs to start developing new sustainable ways to produce fuels. If these fuels cannot be 'zero carbon' then they should be as 'carbon neutral' as possible.

There is one major chemical process on the planet that does use solar energy to power to synthesis of fuel and this is photosynthesis. So is it possible to learn from photosynthesis to devise novel strategies to use solar energy to make fuels, especially those that can be used for transportation?

Although, at present we do not have all the detailed information that is needed in order to produce such systems it is possible from a consideration of the essence of photosynthesis to start a long the path towards succeeding in this aim. Photosynthesis can be divided into four key partial reactions [1]. These are light-harvesting (light-concentration), using this concentrated light-energy to separate charge across a membrane, accumulation of positive charges on one side of this membrane in order to extract electrons from water (water splitting) and accumulation of the negative charges on the other side of this membrane in order to do catalysis to produce a fuel (e.g. the conversion of carbon dioxide to carbohydrate)

Jim Barber from Imperial College in London has championed the idea of an artificial leaf. This is an elegant concept that really clearly illustrates the idea of using the photosynthetic blueprint in order to design ways of using solar energy to produce fuels. We will consider in this presentation each of the four key partial reactions of photosynthesis, outlined above, in order to assess where current research is along path to producing fuels from solar energy. We will describe both our current approaches and where we think the major bottlenecks are.

[1] ESF report on "Harnessing solar energy for the production of clean fuels". <http://ssnmr.leidenuniv.nl/files/ssnmr/CleanSolarFuels.pdf>



Bioenergetic Studies in the Parisian Area

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In the area south-west Paris is currently built the largest research campus in France. Studies concerning climate, energy and environment constitute an important aspect of this operation. The different facets of this project, whether these concern fundamental or applied research will be detailed, as well as their insertion in largest European initiatives.

Research in bioenergetics performed at the Institute of Biology and Technology of Saclay constitutes the 'bio' branch of this project. They mainly concern

- (i) the design of new, bioinspired, photocatalysts, able to perform reactions involving more than one electron, with the final aim to photodissociate water.
- (ii) design of mutant hydrogenase proteins, (more) resistant to the presence of hydrogen
- (iii) the characterisation of the cascade of events following stress in oxygenic organisms, which ultimately result in the quenching of the incoming solar energy : these reactions occur whether these organisms are submitted to light-, drought- or cold-stress, and constitute a serious limitation to biomass production. We have recently characterised the proteins involved in this quenching process, as well as the molecular mechanisms which allow an efficient trapping of the excess excitation energy [1-3]. Recent advances in this field will be described, in plants, diatoms and cyanobacteria.

References

- [1] Pascal AA, Liu ZF, Broess K, van Oort, B, van Amerongen H, Wang C, Horton P, Robert B, Chang W and Ruban A (2005) *Nature* 436 (7047): 134-137. (128)
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Combining Technology with Biology for Efficient Energy Production and Use

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The anthropocene era is characterized by an increasing imbalance in many Earth systems¹. Although our understanding of the coupling between the climate system and human activity is incomplete, there is little doubt that the climate system is linked to CO₂ emissions from fossil fuel production and use. Conservation and increases in energy transformation efficiency can play key roles in reducing emissions. Progress in these efforts is increasingly urgent as the first world responds to the challenge of convergence of Earth's developmentally diverse peoples to sustainability. Biological energy transduction processes address the issue of efficiency by offering examples of elegant machinery, composed of earth-abundant materials, that operates efficiently and essentially isothermally. Moreover, biological systems exhibit repair, self-assembly and replication – features that so far remain elusive to human-engineering of devices. Biological mainstream processes that might be advantageously incorporated into emerging energy technologies include catalysts for O₂/H₂O, H⁺/H₂, CO₂/CH₂O redox reactions, reactions involving making/breaking carbon-carbon bonds, the redox chemistry of nitrogen, and many others. Focusing on solar energy conversion, photosynthesis inspires us to imagine technologies that would convert solar energy to fuel at rates commensurate with human use. Aspects of photosynthetic machinery that are important to future solar technologies include energy transfer, photoinduced electron transfer at molecular heterojunctions, catalysis, protective mechanisms, and control networks. In addition to the design, synthesis and assembly of constructs that carry out such processes, artificial photosynthesis can define the design parameters to be used in the nascent field of synthetic biology to make vast, much needed improvements in the energy yield of photosynthesis^{2,3}. Several bio-inspired constructs for solar energy conversion have been assembled and will be presented. In one, a photobiofuel cell uses artificial reaction centers, visible light and two enzymes to reform biological substrates such as ethanol into hydrogen⁴. This system interfaces redox chemistry with electromotive force at two junctions, and demonstrates two methods for coupling biological redox catalysts with emf. In a second system, solar-driven water oxidation using an IrO₂ catalyst and an external boost of about 0.2 V allows the electrons to combine with protons, producing hydrogen at the cathode⁵. We have developed energy and electron transfer-based models for incorporation of control features into artificial systems^{6,7}.

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Artificial photosynthetic systems for reduction of NADP model compounds and CO₂

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Both problems of the global warming and shortage of the fossil fuels have brought about great interest in artificial photosynthesis. In photosynthesis of green plants, electrons captured from water using solar energy are stored into the coenzyme NADP. The product NADPH is used for reduction of CO₂ as a reductant in the Calvin cycle. Therefore, development of both photocatalysts for reduction of NADP and CO₂, which require two-electron (hydride) reduction, should be important targets in the field of the artificial photosynthesis.

I report our recent results about architectural investigation of such photocatalysts.

We have developed highly efficient photocatalytic systems using the rhenium(I) complex(es) as either photocatalyst or catalyst for CO₂ reduction.¹ I will focus on the following systems in my talk.

- (1) Development of the most efficient photocatalytic system with two different Re(I) complexes ($\Phi_{\text{CO}} = 59\%$).^{1a}
- (2) Architecture of supramolecular metal complexes with both Ru(II) and Re(I) complexes as photosensitizer and catalyst, respectively.²

Ordinary photocatalysts, which initiate intermolecular electron transfer, is useless for reduction of NADP model compounds to the corresponding 1,4-dihydroforms because of rapid coupling reactions of the one-electron reduced radicals of the models.

- (3) We have developed a novel type of photocatalytic systems which can drive only hydride reduction of an NADP model compound with high selectivity and efficiency.³

References

- 1 (a) *J. Am. Chem. Soc.*, **2008**, *130*, 2023-2031. (b) *J. Am. Chem. Soc.*, **2005**, *127*, 15544-15555. (c) *Res. Chem. Intermediat.* **2007**, *33*, 37-48. (d) *J. Photochem. Photobiol. A: Chem.*, **1996**, *96*, 171-174. (e) *Organometallics*, **1997**, *16*, 5724-5729. (f) *J. Chem. Soc., Dalton Trans.*, **1997**, 1019-1023.
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Correlation of Electronic Structure and Reactivity- The Case of Oxidized Metal Salens

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The interplay of redox-active transition metal ions and pro-radical ligands in metalloenzyme sites is an area of considerable research interest. Galactose oxidase (**GOase**), a mononuclear copper enzyme with a Cu(II)-phenoxyl radical active oxidant, is the archetypical example. The simplicity of the single copper active site of the enzyme galactose oxidase[1], which functions by catalyzing the oxidation of primary alcohols to aldehydes while reducing dioxygen to hydrogen peroxide, has inspired efforts to develop small molecule mimics capable of mild and selective alcohol oxidation. To this end, we have investigated the chemistry of a series of simple oxidized bis-phenoxide metal complexes, which demonstrate that ostensibly small variations of the ligand structure affect the locus of oxidation. Oxidation of the neutral bis-phenoxide complexes with a variety of one electron oxidants leads to highly coloured oxidized metal complexes in solution; the nature and stability of these species has been found to depend on the solvent and counterion present.[2,3] Integration of information from near infrared spectroscopy, magnetic susceptibility, electrochemistry, resonance Raman spectroscopy, x-ray crystallography and x-ray absorption spectroscopy provide critical insights into the nature of the localization/delocalization of the oxidation locus. An intriguing example is the one-electron oxidized form of [Cu(II)**Sal**] (**Sal** = (*rac*)- *N,N'*-bis(3,5-di-*tert*-butylsalicylidene)cyclohexane-1,2-diamine) that is a Cu(III) species in the solid state, yet exists in a spin equilibrium in solution between the ligand-radical-Cu(II) species and Cu(III) forms, demonstrating the near isoenergetic nature of these two electronic descriptions. In addition, we have investigated a series of group 10 metal complexes (Ni, Pd, Pt), probing the effect of the metal ion bridge on the degree of electronic communication between the two redox-active phenolate ligands.[4] An account of our most recent work with asymmetric ligands, thereby limiting ligand radical delocalization, will also be described.

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Photoelectrochemical Simulation of Energy Conversion in the Photosynthetic Primary Processes and Design for Film-type High-efficiency Dye-sensitized Solar Cells

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Dye-sensitized solar cell (DSSC) uses environmentally benign materials and low-cost printing processes. In DSSC, Ru bipyridyl complex dyes, which had been also employed by M. Calvin's group to mimic the photosynthetic water splitting reaction, are now capable of yielding high efficiency in solar energy conversion up to 12%, which well competes with amorphous Si solar cells. We have been focusing on developing film-type DSSCs using plastic substrates to realize a leaf-like flexible cell. The conversion efficiency of 5-7% has been achieved using organic dye sensitizers and mesoporous TiO₂ as semiconductor [1]. Fig. 1 shows a plastic DSSC which allows transmission of red light to activate plant photosynthesis while absorbing green light for power generation. Many natural dyes also function as good sensitizers to TiO₂ and ZnO. As a metal-free chlorophyll derivative, chlorin-e6, is useful for designing a DSSC (green color) of 4.4% conversion efficiency, which exhibits an action spectrum of photocurrent similar to that of natural photosynthesis (Fig. 2)[2]. Environmentally benign photovoltaic cells are constructed based on our low-temperature electrode fabrication techniques. Proof-of-concept experiments, including manufacture of large-area modules and durability tests, are in progress.

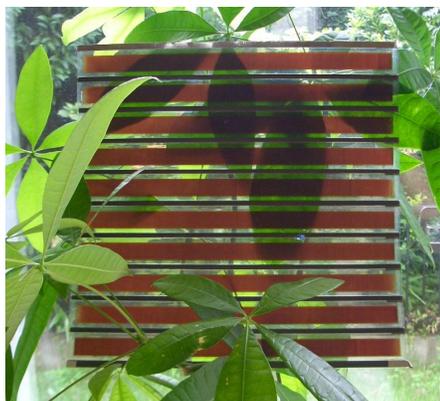


Fig. 1 Full-plastic DSSC module with a series DC connection for a high voltage output of 7.2V

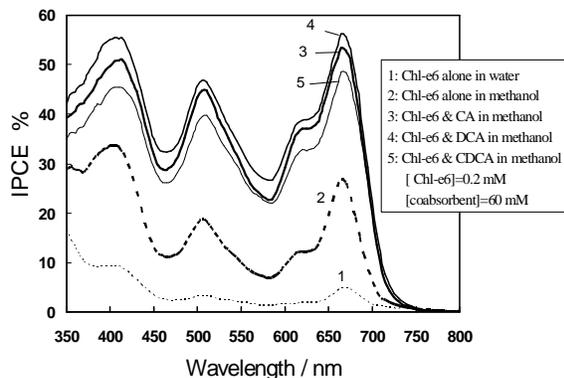


Fig. 2 Action spectra of chlorin-e6 sensitized DSSC. The dye absorption on TiO₂ was done with various concentrations of co-absorbers (cholic acid, CA). Electrode substrate was FTO-coated glass.

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DESIGN OF PHOTOELECTROCHEMICAL CELLS FOR THE SPLITTING OF WATER AND FUEL PRODUCTION

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The long-term objective of our research is the design of bioinspired schemes that couple solar energy conversion to the oxidation of water and the subsequent use of the reducing equivalents to synthesize energy-rich compounds, such as hydrogen or fuels based on reduced carbon. In order to establish the design principles for a tandem, two junction (or threshold) photocell, we are assembling Grätzel-type photoelectrodes that model photosystems I and II (PSI and PSII). The photoanode model of PSII will contain a mimic of the donor side (water oxidizing side) of PSII reaction centers. In PSII, tyrosine Z (Tyr_Z) mediates charge transport between the photo-oxidized primary donor (P680⁺) and the oxygen-evolving complex (OEC). The oxidation of Tyr_Z by P680⁺ likely occurs with the transfer of the phenolic proton to a hydrogen-bonded histidine residue (His190). This coupling of proton and redox chemistry is thought to poise the Tyr_Z oxidation potential between those of P680⁺ and the OEC.

We have prepared a bioinspired system (BiP-PF₁₀) consisting of a high oxidation potential porphyrin (PF₁₀, 1.59 V vs. NHE, a model of P680) that is covalently attached to a benzimidazole-phenol pair (BiP) that mimics the Tyr_Z-His190 pair in PSII. Electrochemical studies show that the phenoxyl radical/phenol couple of the model system is chemically reversible with a midpoint potential of 1.24 V vs. NHE and is therefore thermodynamically capable of water oxidation. When the BiP-PF₁₀ construct is attached to TiO₂ nanoparticles and excited with visible light, it undergoes photoinduced electron transfer. Electrons are injected into the semiconductor and the corresponding holes are localized on either the porphyrin (BiPPF₁₀^{•+}-TiO₂^{•-}) or the phenol (BiP^{•+}-PF₁₀-TiO₂^{•-}). EPR provides a clear spectroscopic picture of these processes.¹

The photoelectrode model of PSI will be sensitized by low potential naphthalocyanines or phthalocyanines, which absorb light in the near IR region of the spectrum. Upon photoexcitation, these dyes are designed to inject electrons into semiconductors having sufficiently negative conduction bands to effectively drive the reduction of protons to hydrogen at a cathode. The semiconductor will be electrically wired to a cathode suitable for hydrogen production: either a metal electrode (Pt or Ni) or a hydrogenase-modified carbon electrode. Cyclic voltammetric studies of *Clostridium acetobutylicum* [FeFe]-hydrogenase (HydA) films on carbon electrodes demonstrate cathodic proton reduction and anodic hydrogen oxidation. The high surface area carbon felt/hydrogenase electrode shows promising properties as the cathode of the photoelectrode mimic of PSI.²

This arrangement of two photosystems operating in tandem has the potential of being much more efficient than natural photosynthesis because the artificial PSI and PSII, in contrast to their natural counterparts, do not compete for the same region of the solar spectrum.

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Structure around Oxygen-Evolving Mn_4O_xCa -Cluster of Photosystem II Complex from *Thermosynechococcus vulcanus*

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Photosystem II (PSII) performs light-induced electron transfer and water-splitting reactions, which lead to the formation of molecular oxygen essential for almost all of the life on the earth. The components of PSII from cyanobacteria include 17 membrane-spanning subunits, 3 hydrophilic, peripheral subunits, and over 90 cofactors such as chlorophylls, Mn, Ca, Cl, Fe, plastoquinones, carotenoids, and lipids, which give rise to a total molecular mass of 350 kDa for a monomer. The structure of PSII has been reported at 3.8-2.9 Å resolution by X-ray crystallographic analyses of PSII isolated from two thermophilic cyanobacteria, *Thermosynechococcus elongatus* and *T. vulcanus*. In the structural model of PSII from *T. elongates* most recently reported by Zouni and Saenger's group in Berlin [1], the locations of all 20 subunits and 96 cofactors were identified. One of the cofactors is a chloride anion (Cl⁻), known to be essential for oxygen evolution of PSII and closely associated with the Mn_4O_xCa -cluster. The anion locates in one of the channels proposed for the transport of protons. However, the structure of Mn_4O_xCa -cluster itself is still unclear because the resolution of 2.9 Å is insufficient to resolve the positions of Mn, Ca, and oxygen atoms independently, and because the cluster is highly sensitive to X-ray radiations so that the intact cluster structure is easily destroyed as shown by the technique of Extended X-ray Absorption Fine Structure. In order to overcome the X-ray damage problem of PSII crystals, a damage reducing protocol was adopted at the SPring-8 beamlines for the diffraction intensity measurements using relatively large PSII crystals. Discussions will be given from this point of view. Another point of our presentation will be on the number of Cl⁻-binding site. We substituted Cl⁻ with Br⁻ or I⁻ in the crystals of PSII from *T. vulcanus*, and analyzed the crystal structures [2]. The results clearly showed that there exist two anion-binding sites in one monomer of PSII, instead of one site as reported by the Berlin group. The two sites were located in positions surrounding the Mn_4O_xCa -cluster at equal distances to the metal cluster. Possible function of the second binding site will be discussed.

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Manganese-Polyoxometalate Architectures: Towards Water Oxidation Catalysts Inspired by Photosystem II

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Photo conversion of water provides a route leading to reducing equivalents of NADPH by photosynthetic organisms and this is an extremely efficient process in which molecular oxygen is generated as a by-product. The first stages of the process take place in the WOC (water-oxidising complex) present in photosystem II. At the heart of this complex is an inorganic cofactor; a cubane comprising three manganese centres and a calcium centre connected by oxo, or oxo-derived bridges. It is at this site where the oxidation of water is thought to occur via four proton coupled electron transfer events in this redox-active cubane. Although a number of catalytically active coordination model compounds have been synthesised, their absolute activity, stability, and turn over can be limited due to the stability of the organic groups associated with the cluster.

Here we present an approach to substitute the organic directing ligands by a more robust polyoxometalate clusters.¹ Polyoxometalates are molecular metal oxides based upon a variety of metals (either W, Mo, V, Nb) and represent interesting candidates not only to their stability, but also due to their tunable redox potentials and ability to take part in multiple electron transfer processes. In our recent work we have shown that manganese substituted POMs display a fantastic variety of architectures, and one very important cluster recently revealed by us, has both interesting electrochemical and magnetic properties,² see Figure 1.

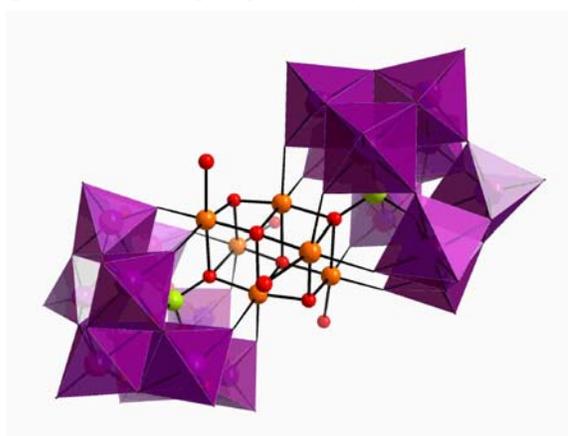


Figure 1. The POM-Mn cluster: $\{[XW_9O_{34}]_2[Mn^{III}_4Mn^{II}_2O_4(H_2O)_4]\}^{12-}$. Colour scheme: purple polyhedra: WO_6 ; orange spheres: Mn; green spheres: X (Si or Ge), red spheres: oxygen.

In this talk I will explain the background behind molecular metal oxide clusters (Polyoxometalates), their architecture,³ and their physical properties and postulate some new directions that could allow the assembly and fabrication of new catalyst-devices that could oxidise water.

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Green Oxidation Catalysts

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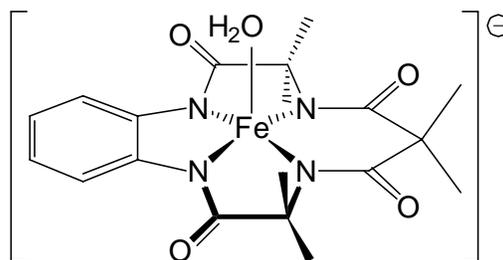
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Oxidation chemistry plays a central role in many large industrial processes. In situations where chlorine-based oxidants are used in conjunction with organic compounds the formation of potentially harmful organo-chlorine compounds is often an inevitable side reaction. Inexpensive, alternative oxidants that do not pose this problem include oxygen and hydrogen peroxide, and accordingly these are often referred to as “green oxidants”. However, reactions under mild conditions with these reagents are usually very slow and indiscriminate. There is therefore an important need to develop suitable catalysts that will improve the efficiency and effectiveness of these oxidants. Prof. Collins and his group have developed a class of iron complexes known as TAMLs[®] that catalyse oxidations with hydrogen peroxide [1]. These catalysts are water soluble and are highly effective at very low concentrations. In collaboration with Prof. Collins we have studied the possibility of using the TAML[®]/hydrogen peroxide oxidation system to replace the use of chlorine-based bleaches in the pulp and paper industry and also as a remediation treatment for waste-water streams [2]. An important aspect of the tetra-amido macrocyclic ligands that are at the heart of the TAML[®] catalysts is that they are amenable to chemical modification. In collaboration with Prof. Collins we have explored a number of these modifications and have recently developed a new type of TAML[®] complex that has quite different but complimentary properties to the original class of TAMLs[®]. In this lecture the use of TAML[®]/hydrogen peroxide as a green oxidation system will be discussed and our new developments in the synthesis and study of modified TAMLs[®] will be presented.



Iron TAML[®] complex

[1] T. J. Collins, *Acc. Chem. Res.* **2002**, *35*, 782-790

[2] T. J. Collins, J. A. Hall, L. D. Vuocolo, N. L. Fattaleh, I. Suckling, C. P. Horwitz, S. W. Gordon-Wylie, R. W. Allison, T. J. Fullerton, L. J. Wright. “The activation of hydrogen peroxide for selective, efficient wood pulp bleaching in “*Green Chemistry: Challenging Perspectives*” P. Tundo, ed., Oxford University Press, Oxford, pp 79-105, 2000.



New Platforms for Probing Early Transition Metal Trends for Bimetallic Dinitrogen Activation and N≡N Bond Cleavage

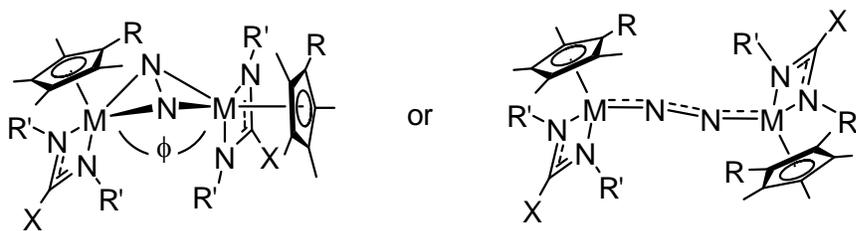
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At the heart of potential solutions to many existing and future problems associated with expansion of the global population by an estimated 3 to 4 billion additional people over the next 50 yrs are scientific breakthroughs that *must be made in the near term* to increase the 'clean technology' quotient of many industrial chemical processes that can simultaneously reduce energy and environmental requirements and consequences. In this respect, the current energy and environmental costs for existing nitrogen-based fertilizer production employing the Haber-Bosch (HB) process, which converts dinitrogen to ammonia through direct hydrogenation over iron-based catalysts at high temperature and pressure, are quite high, even if presently unavoidable.

Toward the goal of developing more energy-efficient processes involving transition metal-mediated N₂ activation, N≡N cleavage, and N-atom functionalization processes, we initiated a program to systematically investigate the roles played by formal metal oxidation state and dⁿ electron count across several different *ligand-centered iso-structural* (LCIS) series of bimetallic [L_nM]₂(μ-N₂) complexes for the group 4 - 6 metals in which the mode of N₂ coordination and extent of activation might vary, but for which the steric and electronic features of the ligand sphere remain invariant [1,2] This talk will focus on recent results obtained to date for two new families of supporting transition metal ligand environments, monocyclopentadienyl, amidinate (X = Me) (CpAm) and monocyclopentadienyl, guanidinate (X = NMe₂) (CpGu), that appear to be ideally suited for achieving this goal.



M = Ti, Zr, Hf, Ta, Mo, and W
X = Me or NMe₂

- [1] M. Hirotsu, P. P. Fontaine, P. Y. Zavalij, L. R. Sita, *J. Am. Chem. Soc.* **2007**, *129*, 12690-12692.
- [2] M. Hirotsu, P. P. Fontaine, A. Epshteyn, P. Y. Zavalij, L. R. Sita, *J. Am. Chem. Soc.* **2007**, *129*, 9284-9285.

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