

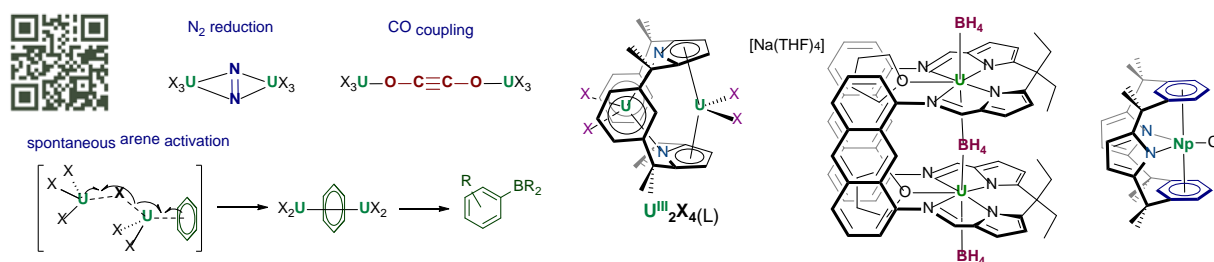
Architectural control of f-block organometallics for small molecule activation

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The activation of small, traditionally inert molecules by metal complexes contributes to our fundamental understanding of metal-ligand bonding and can open up new areas of catalysis. We will present new uranium complexes with simple, bulky ligands that enable the binding and reductive activation of small molecules such as N₂, and can promote C-O cleavage and C-C and C-B bond formation in carbon oxides and aromatic hydrocarbons. We will discuss new results arising from using larger, constraining ligands to preorganise and control these multi-electron reactions.

Arguably more importantly, the study of interactions of f-block cations with softer ligands provides important contributions to the understanding of covalency in f-element ligand bonding that is needed for nuclear waste handling. Time allowing, the electronic structure and magnetic behaviours of sets of new electron-rich, organometallic samarium, uranium and neptunium complexes will be compared.



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Unique Properties of Azaphenylene-based Coordination Materials

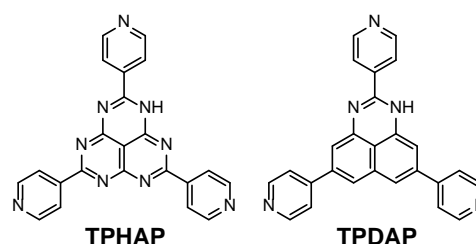
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Abstract

Multi-point weak intermolecular interactions represented by hydrogen bonds and π - π stacking play crucial roles in biologic systems like in the folding events of proteins and enzymatic reactions. As seen in recent examples of functional molecular materials, introducing such weak interactions is one of the crucial techniques to realize unique physical properties such as conductivity, magnetism, chromic behavior, and so on. Our target is to reveal and control the unique properties induced by the metastable frameworks or molecular arrangements which can be stabilized by multi-point weak intermolecular interactions. Here, the azaphenylene-based multi-interactive molecules which were designed for effective trapping of metastable species and utilization of azaphenalenenes for unique coordination molecular systems will be shown.¹⁻³ Azaphenalenenes possess wide π -planar structure and maximum six nitrogen atoms which can work as effective hydrogen-bonding and coordination sites. Furthermore, removal of acidic N-H proton can introduce unique electronic properties which are induced by the presence of non-bonding molecular orbital (NBMO) and controlled by changing the number of nitrogen atoms on the molecular skeleton. By introducing three pyridine rings as the additional interaction sites, we prepared tri(4-pyridyl)hexaazaphenalene (TPHAP)^{1,2} and tri(4-pyridyl)diazaphenalene (TPDAP) (Figure).³ Their unique multi-interactive natures realized surface-mediated single crystal structure transformation, humidity-dependent ion conduction involving the formation of nanometer-thick water layer, selective formation of porous coordination networks by controlling electronic states, and so on.



Figure

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Transition-Metal-Catalyzed Direct Aromatic Coupling

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Transition-metal-catalyzed aromatic cross-coupling reactions are highly useful for the construction of various organic fine chemicals including pharmaceuticals and organic functional materials. The conventional methods, however, usually require the pre-activation of aromatic substrates such as stoichiometric halogenation and metalation before the coupling event, which increases the steps leading to target molecules and yields inevitable salts as byproducts. In order to cope with these problems, catalytic direct coupling reactions on aromatic substrates through C(sp²)-H bond activation/cleavage have recently been one of the most intensive subjects in the area of organometallic catalysis. In this symposium, our efforts for developing direct aromatic and heteroaromatic coupling reactions by using a number of transition metals as catalysts will be presented.¹

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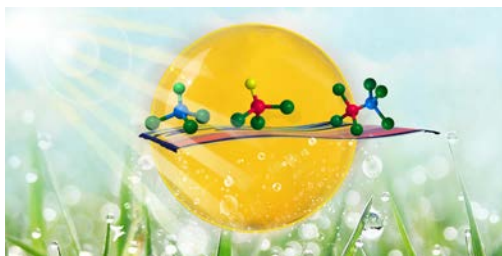
Artificial Photosynthetic Systems for Chemical Transformation

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With the increasing concern over the global energy crisis and the greenhouse effect caused by carbon dioxide emission, the development of carbon-neutral and renewable-energy solutions has attracted considerable interest in both the scientific and industrial communities. Solar energy conversion via natural or artificial photosynthesis requires three main components (Scheme 1). First, antenna/reaction center complexes absorb sunlight and convert the excitation energy to electrochemical energy (redox equivalents). Then, a water oxidation complex uses this redox potential to catalyze conversion of water to protons, electrons stored as reducing equivalents, and oxygen. A second catalytic system uses the reducing equivalents to make fuels such as carbohydrates, lipids, or hydrogen. In this presentation, we will compile the following four stories to illustrate a few approaches that may be useful in the design of artificial photosynthetic systems for chemical transformation. (1) Artificial photosynthetic systems for hydrogen evolution by [FeFe]-hydrogenases mimics; (2) Artificial photocatalysts made by earth-abundant metal salts and quantum dots *in situ* under visible light irradiation; (3) Artificial quantum dots photocathodes for hydrogen evolution by water-splitting under visible light irradiation; (4) Artificial photosynthetic systems for chemical transformation under visible light.

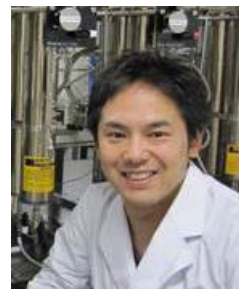


Scheme 1. Artificial photosynthetic system for solar energy conversion

Molecular Catalysts Designed for Water Oxidation

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Water oxidation ($2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$) is considered the main bottleneck in the production of chemical fuels from sunlight and/or electricity. In nature, the oxidation of water is efficiently catalysed by the oxygen-evolving complex (OEC) in photosystem II (PSII). Because extraction of the OEC is extremely difficult, various synthetic molecular catalysts have been investigated over the last decades.^{1–3} However, the development of efficient, robust and abundant metal-based molecular catalysts remains a challenge. In this work, we show a water oxidation reaction catalysed by a pentanuclear iron complex.⁴ Electrochemical analysis revealed that the pentairon complex exhibits rich redox flexibility with six different oxidation states between Fe^{II}_5 and Fe^{III}_5 , in which the Fe^{III}_5 state is the active species for oxidising water. A computational investigation indicated that the O-O bond formation proceeds from the mixed-valence $\text{Fe}^{\text{II}}_2\text{Fe}^{\text{III}}(\text{Fe}^{\text{IV}}=\text{O})_2$ intermediate with a reaction barrier of less than 10 kcal mol⁻¹. The turnover frequency of the water oxidation catalyst was determined to be 1,900 s⁻¹, which is considerably greater than that of the OEC (100–400 s⁻¹). Our findings indicate that efficient water oxidation catalysts can be created based on multinuclear iron complexes with redox flexibility and adjacent water-activation sites.

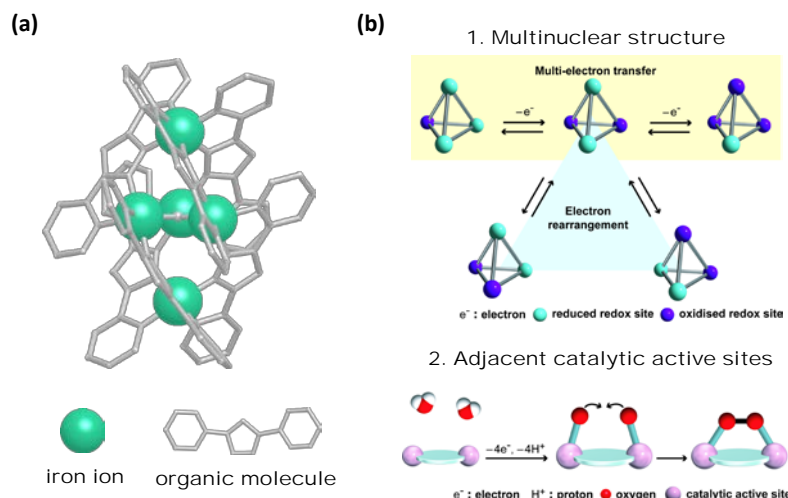


Figure 1. Structure (a) and characteristics (b) of the Fe_5 catalyst.

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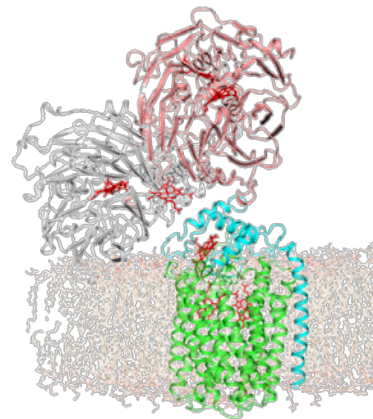
NO dynamics in Biology: its generation and decomposition

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Denitrification is a kind of anaerobic respiration of microorganisms (denitrifier), in which nitrate NO_3^- and nitrite NO_2^- are reduced to dinitrogen N_2 as follows; $\text{NO}_3^- \rightarrow \text{NO}_2^- \rightarrow \text{NO} \rightarrow \text{N}_2\text{O} \rightarrow \text{N}_2$. Each step can be catalyzed by metalloproteins such as nitrate reductase Nar, nitrite reductase Nir, nitric oxide reductase NOR and nitrous oxide reductase N_2OR . Since nitric oxide NO, which is generated in the reduction of NO_2^- by Nir ($\text{NO}_2^- + 2\text{H}^+ + \text{e}^- \rightarrow \text{NO} + \text{H}_2\text{O}$), exhibits a high cyto-toxicity, it must be immediately decomposed to N_2O by NOR ($2\text{NO} + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O}$). Bacterial NOR is a membrane-integrated protein and has a binuclear complex consisting of heme *b* and non-heme iron (Fe_B) as a catalytic center. In 2010 and 2012, we reported crystal structures of cytochrome c dependent NOR (cNOR) from *Pseudomonas aeruginosa* and quinole dependent NOR (qNOR) from *Geobacillus stearothermophilus*.^{1,2} Most recently, we also determined the crystal structure of the Nir-cNOR complex (Figure), which is a system to effectively decompose the highly toxic NO without diffusing it into cell after its formation by Nir. Indeed, mutation of the amino acid residues located at the Nir-cNOR interface significantly affected the growth of denitrifier under denitrification condition. In addition, to elucidate the reaction mechanism of NOR, we could characterize the coordination structure of the short lived intermediate appeared during the NOR enzymatic reaction by time-resolved IR spectroscopy, in which two NO molecules are shared by heme *b* and Fe_B , supporting the *trans* mechanism for the NO reduction.



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Talk Title: Where the Rubber Meets the Road - polyMOFs

Presenter: Seth M. Cohen, University of California, San Diego

Abstract

As porous, crystalline solids, metal-organic frameworks (MOFs) have limited options for materials processing and fabrication. To alleviate this limitation, different strategies to integrate MOFs with processible polymer materials have been explored, such as the use of mixed matrix membranes (MMMs). The direct preparation of porous materials from polymers is challenging because the packing of polymer chains results in a dense, non-porous arrangement. However, we demonstrate the transformation of an amorphous, linear, non-porous, flexible organic polymer into a 3-dimensional, highly porous, crystalline solid, as the organic component of a MOF. A polymer with aromatic dicarboxylic acids in the backbone functioned as a polymer-ligand upon annealing with metal ions to generate a polymer-metal-organic-framework (polyMOF). These materials uproot the dogma that MOFs must be prepared from small, rigid ligands. Similarly, polyMOFs contradict conventional polymer chemistry by demonstrating that linear and amorphous polymers can be readily coaxed into a highly crystalline, porous, 3-dimensional structure via coordination chemistry. polyMOFs are compatible with a variety of MOF architectures including IRMOF-1 type, Cu-paddlewheel type, and UiO-66 type structures. polyMOFs demonstrate interesting gas sorption behavior and demonstrate exceptional water stability attributed to the hydrophobicity of polymer ligands, as well as the cross-linking of the polymer chains within the MOF. Overall, the polyMOF strategy shows promise as a new class of materials that bridge the gap between polymers and porous solids. We are also examining the use of block copolymers to form polyMOFs in order to achieve polyMOF materials with truly polymer-like processing properties, but with high surface areas reminiscent of MOFs.

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Polymer Chemistry in MOFs

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Recently, Metal-Organic Frameworks (MOFs) composed of metal ions and organic ligands have been extensively studied. The characteristic features of MOFs are highly regular channel structures, controllable channel sizes approximating molecular dimensions, and designable surface functionality. Use of their regulated and tunable channels for a field of polymerization allows multi-level controls of resulting polymer structures.¹ In addition, construction of nanocomposites between MOFs and polymers provides unprecedented material platforms to accomplish many nanoscale functions.¹

Controlled radical polymerization of vinyl monomers was attained in MOF nanochannels, showing many remarkable effects of pore size, shape, and functionality on the structures of resulting polymers.² For example, stereo- and regioregularity of polymers could be systematically controlled depending on the pore structure.^{2b-d} Controlled uniaxial alignment of vinyl polymer chains was achieved by host-guest cross-polymerization.^{2e} Use of MOFs as removable templates was a promising method for the mixing of immiscible polymer pairs at the molecular level.^{2f} Recently, we have also developed radical polymerization using porous organic cages with dynamic and responsive packing structure, showing enzyme-mimetic behaviors that cannot be attained in conventional rigid hosts.³

Other than vinyl polymers, a variety of functional polymers, such as bio(compatible)polymers⁴, inorganic polymers⁵, and electroactive polymers⁶, could be prepared/incorporated in MOFs, providing distinctly different properties to those prepared in the bulk state because of the formation of specific polymer assemblies and conformations.

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Elements Strategy for New Nano-Materials Based on DOS Engineering by Inter-Element Fusion

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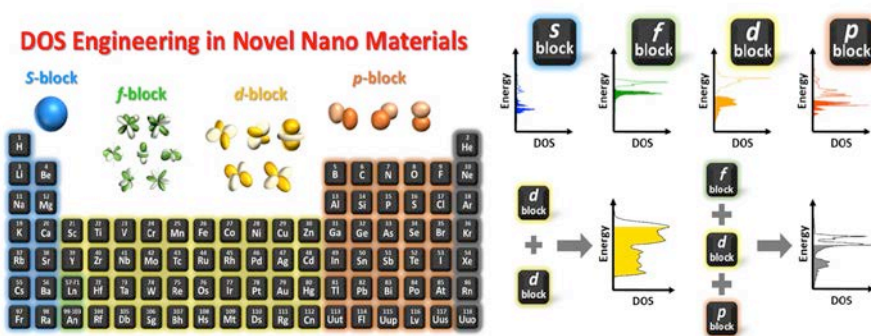
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Of 118 elements, only about 80 elements are stable, nonradioactive, and widely used in our society. Based on “elements strategy”, we need to make full use of the 80 elements to create innovative materials. Furthermore, there is a strong demand from society that the use of rare or toxic elements should be reduced or replaced. Modern science and technology could create higher-performance materials even while replacing or reducing minor or harmful elements through the combination of more abundant elements.

The property of element is correlated directly with its electron configuration. In a solid, the density of states (DOS) at the Fermi level affects the physical and chemical properties. The method of alloying elements has been used to improve the properties of materials for many years. In particular, the solid-solution-type alloy is advantageous because tuning the compositions and/or combinations of the constituent elements can continuously control the properties. However, the majority of bulk alloys are of the phase-separated type under ambient conditions, where constituent elements are immiscible with each other. To overcome the challenge of the bulk-phase metallurgical aspects, we have focused on the nanosize effect and developed methods involving “non-equilibrium synthesis” or “a process of hydrogen absorption/desorption”. We propose a new concept of “density-of-states engineering” for the design of materials having the most desirable and suitable properties by means of “inter-element fusion”.

Novel solid-solution alloys of Pd–Pt, Ag–Rh, and Pd–Ru¹⁾ systems in which the constituent elements are immiscible in the bulk state are presented and discussed. Our present work provides a guiding principle for the design of a suitable DOS shape according to the intended physical and/or chemical properties and a method for the development of novel solid-solution alloys^{2), 3)}.

DOS Engineering by Inter-Element Fusion



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