

# Interfacial Synthesis of Coordination Nanosheets and Their Functions

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Single-layer 2D materials have attracted much attention because of their unique physical and chemical properties. We have synthesized coordination nanosheets (CONASHs) comprising metal ions and organic  $\pi$ -ligands by the interfacial coordination reactions.<sup>1,2</sup> For example, a liquid–liquid interfacial reaction of nickel(II) acetate in an aqueous phase with benzenehexathiol in an organic phase produced semiconducting sheets containing bis(dithiolato)nickel moieties with one micrometer thickness. A single-layer nanosheet with 0.6 nm thickness was successfully synthesized using a gas–liquid interfacial reaction. Modulation of the oxidation state and the electronic conductivity of the coordination nanosheet was achieved using redox reactions. Bis(dithiolato)palladium nanosheet was prepared by a modified interfacial method inhibiting the formation of Pd nanoparticles.

A series of multilayered coordination nanosheets comprising 1,3,5-tris(4-(2,2':6',2''-terpyridyl)phenyl)benzene and iron(II) or cobalt(II) ions was synthesized by liquid/liquid interfacial coordination reactions. The resultant nanosheet had a flat, smooth morphology and was several hundreds of nanometers thick. Upon its deposition on an indium tin oxide (ITO) electrode, the nanosheets underwent a reversible and robust redox reaction ( $\text{Fe}^{3+}/\text{Fe}^{2+}$  or  $\text{Co}^{2+}/\text{Co}^+$ ) accompanied by a distinctive color change. Electrochromism was achieved in a solidified device composed of the nanosheet, a pair of ITO electrodes, and a polymer-supported electrolyte. The combination of  $\text{Fe}^{2+}$  and  $\text{Co}^{2+}$  nanosheets in one device deposited on each ITO electrode demonstrated dual-electrochromic behavior.

We also synthesized coordination nanosheets featuring a photoactive bis(dipyrrinato)zinc(II) complex motif by an interfacial reaction between a three-way dipyrin ligand and zinc(II) ions.<sup>7</sup> The bis(dipyrrinato)zinc(II) nanosheet deposited on a  $\text{SnO}_2$  electrode functions as a photoanode in a photoelectric conversion system.

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## Multi-stability based on intramolecular electron transfers

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Multi-stable system, exhibiting switchable electronic states by external stimuli, is a promising candidate for switching devices and memories in the molecular electronics. Although there are numerous examples of multi-stable molecules, the controlled multi-stability still remains challenging. The multi-stability is originating from a close proximity of the energy levels of each electronic states; therefore, the rational control of the Gibbs free energy for the states is required. We report here a series of cyanide-bridged multi-nuclear metal complexes, exhibiting controlled multi-stabilities (Fig. 1).<sup>[1]-[4]</sup> They exhibit external stimuli-induced electron transfers between the metal centers accompanied with spin transitions of the cobalt ions; here we call this phenomenon as electron-transfer-coupled spin transition (ETCST). We systematically investigated the thermal ETCST behavior of a series of cyanide-bridged multi-nuclear complexes, and the transition temperatures can be rationally controlled by chemical modifications. In addition, we have found a light-induced single molecule magnetism in solid state and a protonation-induced ETCST in solution, which are based on the precise control of intramolecular electron transfers. Dimensionally controlled assembly of the ETCST-active molecules will be also presented.

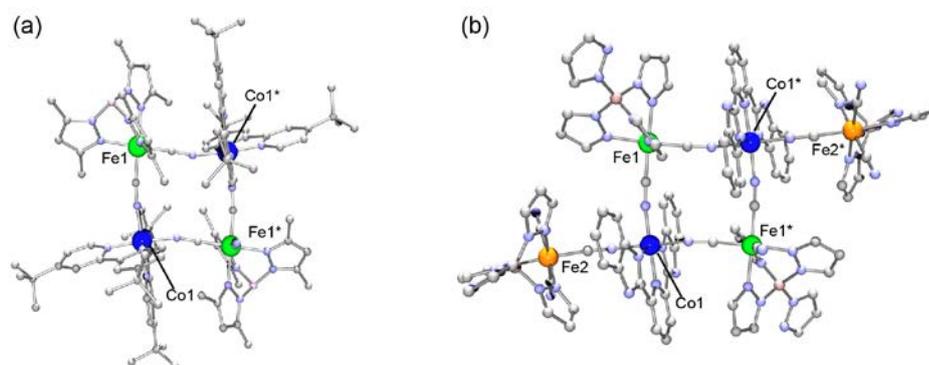


Fig. 1. Structures of cyanide-bridged  $[\text{Co}_2\text{Fe}_2]$  (a) and  $[\text{Co}_2\text{Fe}_4]$  (b) complexes.

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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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Zhenjie Zhang, Ha Thi Hoang Nguyen, Stephen A. Miller, Ann Ploskonka, Jared DeCoste, and Seth M. Cohen\*, "polyMOFs as Water Tolerant Materials for Selective Carbon Dioxide Separations" *J. Am. Chem. Soc.* **2016**, *138*, 920-925. DOI: 10.1021/JACS.5B11034.

# 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.



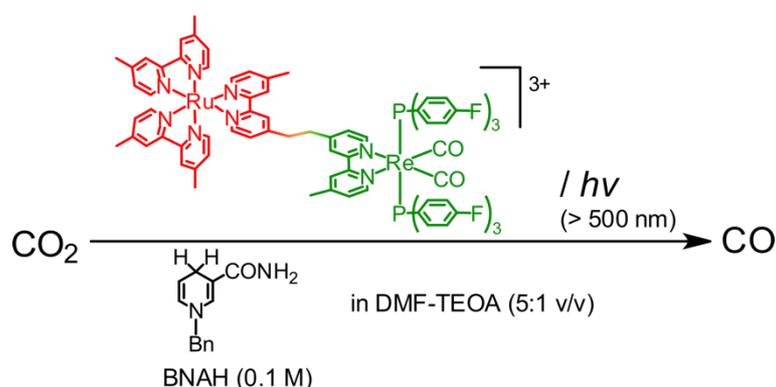
Scheme 1. Artificial photosynthetic system for solar energy conversion

# Photocatalytic CO<sub>2</sub> reduction using multinuclear metal complexes

(Tokyo Institute of Technology) TAMAKI, Yusuke

Reductive conversion of CO<sub>2</sub> into energy-rich compounds using solar light as an energy source has been intensively investigated in recent years as one of promising solutions to global warming and shortage of fossil resources. We have already reported that the multinuclear complexes consisting of [Ru(N<sup>^</sup>N)<sub>3</sub>]<sup>2+</sup> (N<sup>^</sup>N = diimine ligand) photosensitizer unit and Re(I) carbonyl complex as a catalyst unit photocatalyzed the reduction of CO<sub>2</sub> to CO under visible-light irradiation using 1-benzyl-1,4-dihydronicotinamide (BNAH) as a sacrificial electron donor.<sup>[1]</sup> Although these systems exhibited relatively high efficiency, durability, and selectivity, large part of the reaction mechanisms was unclear.

In this presentation, therefore, significant improvement of photocatalytic abilities<sup>[2]</sup> and development of the photocatalytic system with the novel function, i.e., the reduction of low concentration of CO<sub>2</sub>,<sup>[3]</sup> based on the clarification of parts of the reaction mechanisms will be shown. For example, the oxidized products of BNAH were clarified and the electron balance of the photocatalysis was revealed. Since the accumulation of oxidized products of BNAH was found to inhibit the photocatalysis, using a new sacrificial electron donor intensively increased photocatalytic activities.



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# Inorganic materials for photocatalytic water splitting and CO<sub>2</sub> reduction

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Water splitting and CO<sub>2</sub> fixation of uphill reactions can be regarded as artificial photosynthesis, because light energy is converted to chemical energy. In the present paper, we introduce various metal oxide and sulfide photocatalysts and photoelectrochemical cells aiming at artificial photosynthesis.<sup>1)</sup>

Rh and Sb-codoped SrTiO<sub>3</sub> photocatalyst loaded with IrO<sub>2</sub> is active for water splitting into H<sub>2</sub> and O<sub>2</sub> under visible light and simulated sunlight irradiations as a single particle type photocatalyst. This photocatalyst responds to 500 nm.<sup>2)</sup> SrTiO<sub>3</sub>:Rh of a H<sub>2</sub>-evolving photocatalyst and BiVO<sub>4</sub> of an O<sub>2</sub>-evolving photocatalyst construct various type of Z-schematic photocatalyst systems with Fe<sup>3+</sup>/Fe<sup>2+</sup>, [Co(bpy)<sub>3</sub>]<sup>3+/2+</sup>, [Co(phen)<sub>3</sub>]<sup>3+/2+</sup>, and a conductive reduced graphene oxide (RGO) as an electron mediator and even without an electron mediator. It is noteworthy that a sheet photocatalyst consisting of SrTiO<sub>3</sub>:Rh,La and BiVO<sub>4</sub> powders with a Au contacting layer shows a quite high activity.<sup>3)</sup>

Metal sulfide photocatalysts that are normally unstable for water splitting into H<sub>2</sub> and O<sub>2</sub> in the absence of an electron donor can be employed for Z-schematic photocatalyst systems for water splitting. Z-schematic photocatalyst systems combining metal sulfide photocatalysts as a H<sub>2</sub>-evolving photocatalyst with TiO<sub>2</sub> (RGO/TiO<sub>2</sub>)<sup>4)</sup> and BiVO<sub>4</sub>+Co complex (an electron mediator) as an O<sub>2</sub>-evolving photocatalyst show activity for water splitting into H<sub>2</sub> and O<sub>2</sub>.<sup>5)</sup> These photocatalyst materials can also be employed for photoelectrochemical system for solar water splitting.<sup>5,6)</sup>

Ag/BaLa<sub>4</sub>Ti<sub>4</sub>O<sub>15</sub> and Ag/KCaSrTa<sub>5</sub>O<sub>15</sub> photocatalysts with wide bandgaps show activities for CO<sub>2</sub> reduction to form CO and HCOOH in an aqueous medium without any sacrificial reagents.<sup>7)</sup> O<sub>2</sub> evolved with a stoichiometric amount indicating that water reacts as an electron donor indicating that an uphill reaction of CO<sub>2</sub> reduction accompanied with water oxidation was achieved. CuGaS<sub>2</sub>-RGO/BiVO<sub>4</sub> of a Z-scheme photocatalyst system is active for water splitting and CO<sub>2</sub> reduction to CO under visible light irradiation without any sacrificial reagents. This is the first time to demonstrate CO<sub>2</sub> reduction using water as an electron donor in a powdered photocatalyst system with visible light response.<sup>8)</sup>

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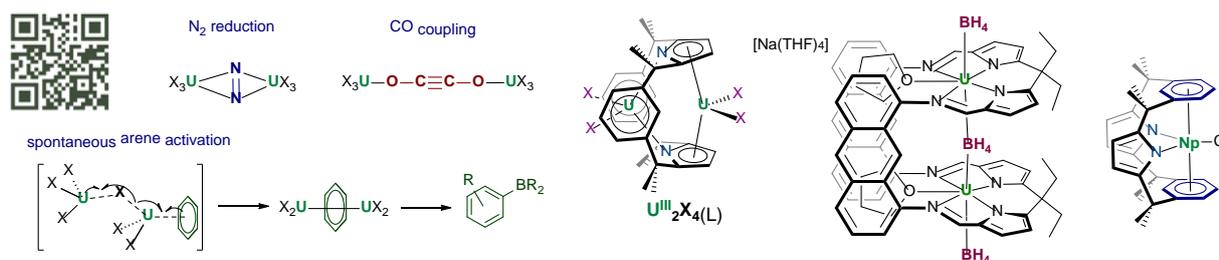
# Architectural control of f-block organometallics for small molecule activation

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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 than enable the binding and reductive activation of small molecules such as N<sub>2</sub>, 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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# Polyaromatic Micelles as New Supramolecular Capsules

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Micelles are spherical assemblies of linear amphiphilic molecules and one of the oldest classes of supramolecules bearing wide-ranging applications. We have recently developed new amphiphilic molecules with a bent polyaromatic framework and two hydrophilic pendants.<sup>[1]</sup> In water, the bent amphiphiles spontaneously and quantitatively assemble into spherical micelles providing polyaromatic shells through effective aromatic-aromatic interactions and hydrophobic effects. Here we report the utility of the polyaromatic micelles as new supramolecular capsules for encapsulating nanocarbons (e.g., fullerene C<sub>60</sub> and carbon nanotube) and metal-complexes (e.g., metallo-phthalocyanines and porphyrins) in water.<sup>[2,3]</sup>

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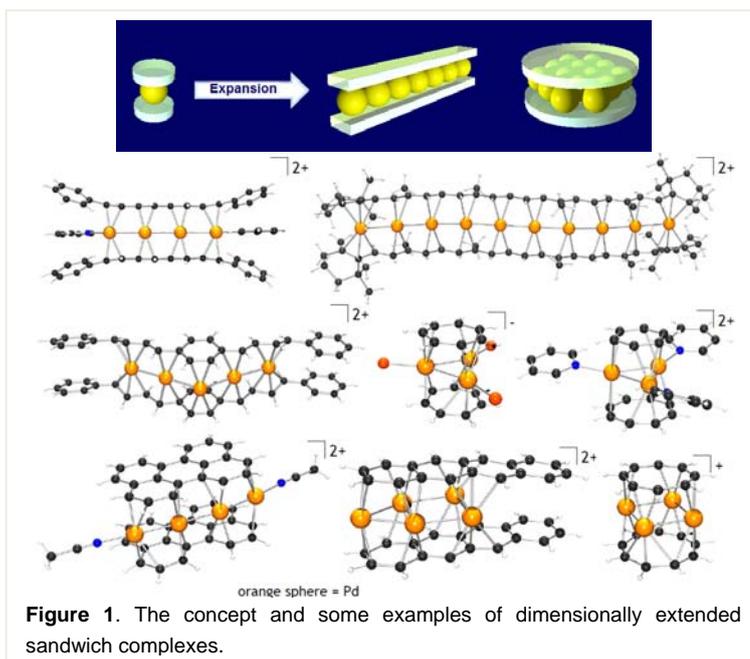
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# Chemistry of Sandwich Clusters

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The sandwich structure is one of the fundamental structural motifs for transition metal complexes. Most of sandwich complexes contain a mononuclear metal moiety between parallel cyclic unsaturated hydrocarbon ligands. On the other hand, it had been difficult to synthesize stable sandwich complexes in which a metal assembly is sandwiched between two parallel unsaturated hydrocarbons. Our group discovered that multinuclear sandwich complexes exist as isolable molecules (Figure 1).<sup>1,2</sup> It has been shown that a wide range of  $\pi$ -conjugated unsaturated hydrocarbons, such as linear  $\pi$ -conjugated polyenes, monocyclic aromatic hydrocarbons, and polycyclic arenes form multinuclear sandwich complexes. Several unique chemical properties of multinuclear sandwich complexes stemming from the ( $\pi$ -conjugated unsaturated hydrocarbon)-(multinuclear metal) hybrid structures have been elucidated.



In this presentation, recent development

in the chemistry of multinuclear sandwich complexes will be overviewed; e.g., tailor-made construction of metal assembly in organometallic sandwich framework,<sup>3,5,6</sup> and elucidation of unique dynamic structural changes induced by redox reactions.<sup>4</sup>

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