

**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, and Seth M. Cohen, "polyMOFs: A New Class of Interconvertible Polymer-MOF Hybrid Materials" *Angew. Chem. Int. Ed.* **2015**, *54*, 6152-6157. DOI: 10.1002/ANIE.201504077.

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.

# Graphene Oxide and Reduced Graphene Oxide Hybrids with Spin Crossover Complexes

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Graphene oxide (GO) is 2D nanosheet, and has many functionality, for example, proton conductivity.<sup>[1]</sup> The GO has negative charge because GO has many oxygen functional groups such as epoxide group, carboxyl group, hydroxyl group and so on.

Therefore, GO is able to combine with positive charge cations such as proton, metal ions, complexes and so on. Furthermore, the hybrids can be prepared by not only electrostatic interaction but also  $\pi$ - $\pi$  stacking or chemical bonding between epoxy and amine groups. After reduction of GO by hydrazine, UV irradiation or annealing, reduced GO (rGO) can be produced, which shows electrical conduction. After reduction of GO hybrids, rGO hybrids also can be produced. In this study, we focus on GO and rGO hybrids with spin crossover (SCO) cations ( $[\text{Fe}(\text{qsal})_2]^+$  (**1**) and  $[\text{Fe}(\text{qnal})_2]^+$  (**2**)). The complexes exhibit a unique SCO behavior depending on counter anions. GO-SCO hybrids (**1**-GO and **2**-GO) and rGO-SCO hybrids (**1**-rGO and **2**-rGO) were synthesized. (Figure 1) **2**-GO and **2**-rGO exhibited gradual SCO behavior. Moreover, a light-induced excited-spin-state trapping (LIESST) effect for **2**-rGO was observed (Figure 2). After reduction of GO hybrids,  $[\text{Fe}(\text{qsal})_2]_n\text{rGO}$  and  $[\text{Fe}(\text{qnal})_2]_n\text{rGO}$  also showed electrical conduction. Graphene-based materials with multi-functionality are presented here for the first time. We succeeded to control the domain size of the SCO complexes on the GO nano sheet. Further we will discuss about other GO hybrids.

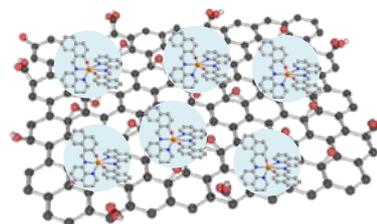


Fig. 1 Structure of GO-SCO hybrid.

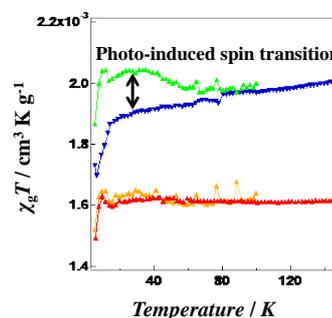


Fig. 2 The  $\chi_g T$  vs temperature behavior for **2**-GO and **2**-rGO hybrids.

After reduction of GO hybrids,  $[\text{Fe}(\text{qsal})_2]_n\text{rGO}$  and  $[\text{Fe}(\text{qnal})_2]_n\text{rGO}$  also showed electrical conduction. Graphene-based materials with multi-functionality are presented here for the first time. We succeeded to control the domain size of the SCO complexes on the GO nano sheet. Further we will discuss about other GO hybrids.

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# Photon Upconversion based on Triplet Energy Migration

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We show exciting research opportunities when the concept of molecular self-assembly meets photon upconversion (UC) based on triplet-triplet annihilation (TTA).<sup>1</sup> In dense dye assemblies, triplet excitons can efficiently migrate and annihilate. Highly efficient photon upconversion has been realized in a wide range of chromophore assemblies, such as non-solvent liquids, ionic liquids, amorphous solids, gels, supramolecular assemblies, liquid crystals, and crystals. The control over their assembly structures allows for unexpected air-stability and efficient upconversion at weak excitation intensity. The introduction of the “self-assembly” concept offers a new perspective in photon upconversion research and triplet exciton science, which show promise for numerous applications ranging from solar energy conversion to chemical biology.

In addition, we would like to introduce our recent progress in the near-infrared (NIR)-to-visible (vis) UC.<sup>2</sup> NIR-to-vis UC is very important for various applications, however, it remains challenging mainly due to the energy loss during the S<sub>1</sub>-to-T<sub>1</sub> intersystem crossing (ISC) of molecular sensitizers. We circumvent this energy loss by employing a sensitizer with direct S-T absorption in the NIR region. Sensitizer-doped emitter nanoparticles are prepared by re-precipitation and dispersed into an oxygen-barrier polymer. The obtained composite film shows a stable NIR-to-vis UC emission based on triplet energy migration (TEM), even in air. A highly efficient UC is observed for this TEM-UC system, expanding the scope of molecular sensitizers for NIR-to-vis UC.

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## Molecular catalysts and photocatalysts towards solar water splitting reactions

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### **Abstract:**

The basic concepts for the molecular catalysis of mononuclear and dinuclear platinum(II) complexes in water reduction to H<sub>2</sub> have been advanced. Our studies involve photochemically, chemically, and electrochemically driven catalysis. Important targets have been to develop molecular catalysts exhibiting an effectively lower overpotential for either water oxidation or reduction process. Platinum(II) complexes had been for a long time rare examples of molecular catalysts promoting hydrogen evolution reaction (HER) when driven with methylviologen radical (150 meV of driving force for HER at pH 5.0) Importantly, the Pt(II)-catalyzed H<sub>2</sub> evolution was reported to undergo via the hydridodiplatinum(II,III) intermediate with the activation barrier lowered by the specific metal-metal bonding interaction. Based on modification of EDTA/Ru(bpy)<sub>3</sub><sup>2+</sup>/MV<sup>2+</sup>/Pt(II)-Catalyst (MV<sup>2+</sup> = methylviologen) for photocatalytic HER, various types of hybrid molecular systems have been developed. These involve dyads, given from a covalent linkage of Ru(bpy)<sub>3</sub><sup>2+</sup> and PtCl<sub>2</sub>(bpy). They behave as single-molecular photocatalysts driving photo-driven water reduction to H<sub>2</sub> by EDTA. Some simple mononuclear Pt(II) complexes, such as those having either Pt(II)Cl(terpy) or Pt(II)Cl<sub>2</sub>(bpy) unit, were also shown to serve as such photo-hydrogen-evolving molecular devices. Introduction of multiple viologen acceptors to such Pt(II) systems led to great improvement in the net photocatalytic performance.

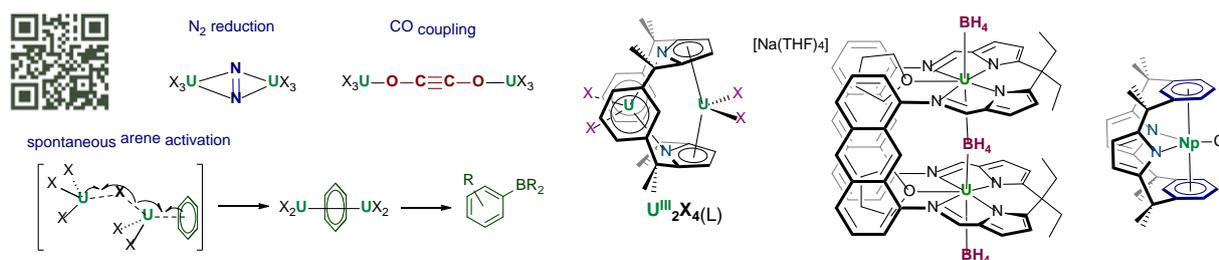
# Architectural control of f-block organometallics for small molecule activation

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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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# Coordination Chemistry of “N-Confused” Expanded Porphyrinoids Toward Near-IR Optical Materials

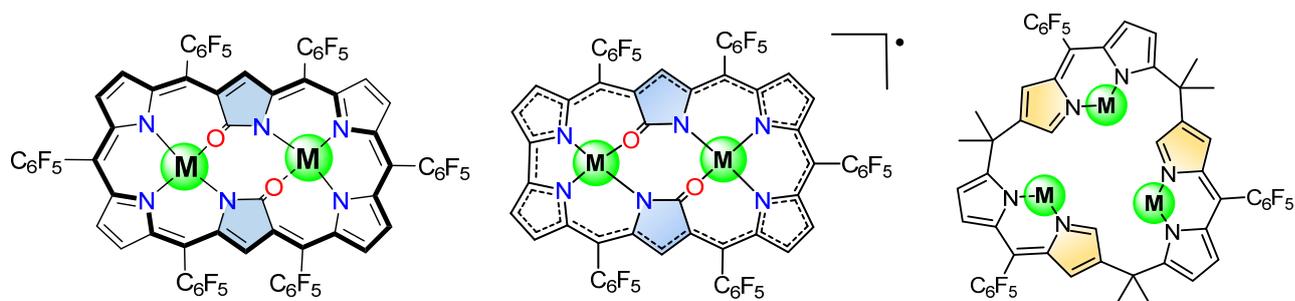
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The chemistry of expanded porphyrins, which are higher-numbered pyrrolic homologues of natural tetrapyrrolic systems, has been intensively explored for the last three decades.[1] Expanded porphyrins exhibit unique structures, electronic properties, and chemical reactivities as being highlighted by the facile realization of Möbius twisted aromatic and antiaromatic systems, stable open-shell  $\pi$ -radicals, and opto-electronic materials in the near-infrared region.[2] In addition, multi-metal coordination ability of the expanded porphyrins is indeed noteworthy; the systems are synthetically useful for the production of unprecedented metal complexes with novel structures and electronic properties and even for triggering irreversible chemical transformations.[3] However, the metalation behavior of standard expanded porphyrins is rather difficult to predict due to the structural flexibility.

In this regard, we have designed new core-modified multi-pyrrolic macrocycles with use of an “N-confusion approach”.[4] The implementation of confused pyrrole rings connected at the  $\alpha$  and  $\beta'$ -positions between the *meso* carbons of the macrocycle allows for the exploration of a new frontier consisting of “porphyrin-like” coordination chemistry. For example, a doubly N-confused dioxohexaphyrin derivative has a laterally expanded planar  $26\pi$  macrocycles with nitrogen-rich vacant sphere, which can afford diverse bis-metal complexes with distinct planar geometries.

We have recently succeeded in synthesizing further structural modified derivatives; i) a core contracted and ii) the hybrid calixphyrin systems for multi-metallic complexes.[5] The peculiar structural effects of N-confused expanded porphyrinoids will be presented.



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# Crystal Engineering of Multicomponent Molecular Puzzles for Photofunction Design

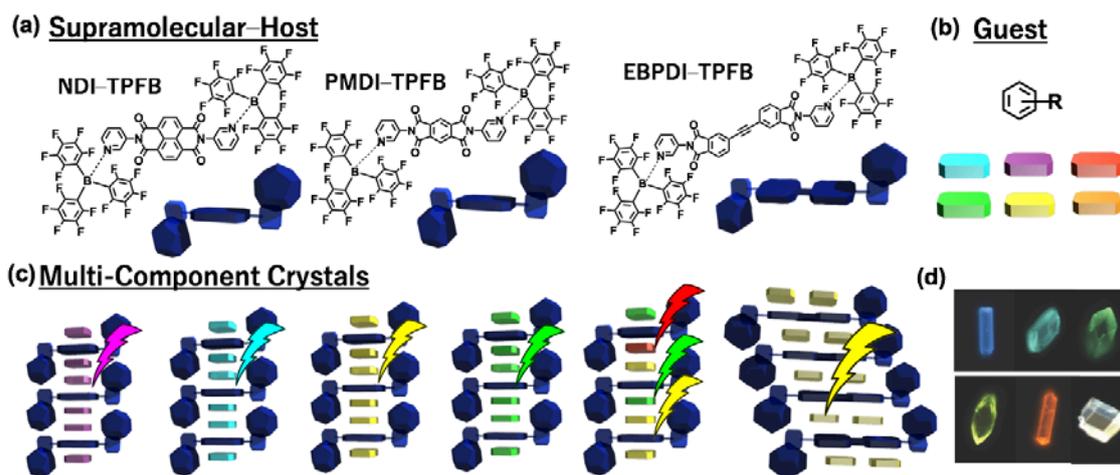
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Multicomponent crystals or co-crystals formed with two or more different molecules have attracted much attention because of their promising applications for advanced materials such as novel optical, electronic and magnetic properties, but their collective behaviors in materials remain poorly understood. In this aspect, supramolecular chemistry and crystal engineering techniques play an important role in providing functional molecular assemblies and crystalline materials. For the sake of this purpose, here we report a set of multicomponent crystals that showed (1) color-tunable (multi-color & white light) and (2) lifetime-controllable (fluorescence & phosphorescence) properties by accommodating aromatic guest molecules into the supramolecular-host molecules as shown in Fig 1. The present study suggests that a rational solution of multicomponent molecular puzzles would be useful for obtaining novel photofunctional solid-state systems.



Light-emitting properties are originated from charge-transfer (CT) interactions between Supramolecular-Host and Guest molecules.

**Fig 1.** Concept of this study (a) Chemical structure of supramolecular-Host (NDI-TPFB, PMDI-TPFB and EBPDI-TPFB). (b) Image of guest molecules, (c) Image of guest-dependent emission properties of multi-component crystals. (d) Microscope images of light-emitting multi-component crystals under UV light irradiation.

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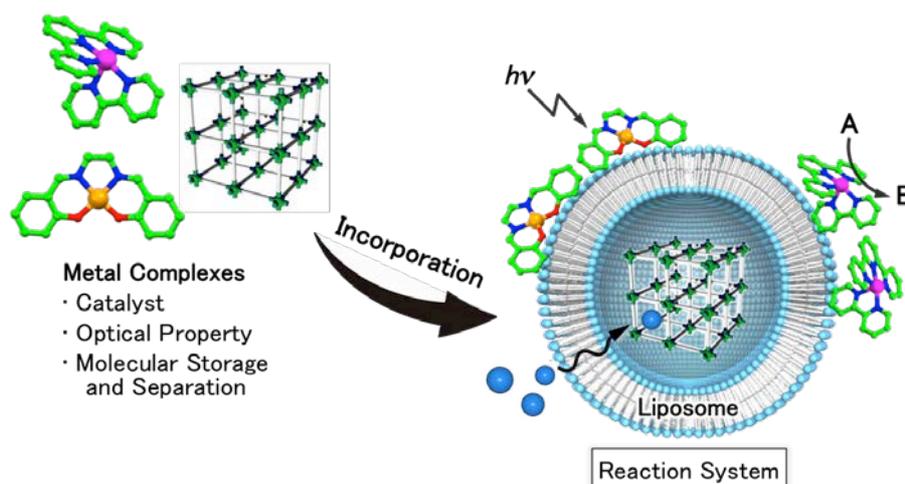
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# Design of Functional Composites based on Liposome and Metal Complex

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Hierarchical integration of various functional components, such as cofactors and enzymes, is achieved using biomembrane and protein assemblies in nature, leading to coupling of different chemical reactions. Artificially creating such multifunctional reaction systems is one of the most considerable topics in current chemistry. Although various chemical reactors consisting of polymers and proteins have been studied, it is still difficult to construct reaction systems in which different chemical reactions occur simultaneously. We focus on liposome, which is an artificially-prepared spherical vesicle composed of a lipid bilayer of phospholipids, as a chemical reaction space. It is expected that different functional molecules co-exist in or on one liposome hierarchically, because a liposome provides four different regions, namely - hydrophilic inner water phase, hydrophobic lipid bilayer, and inner and outer surfaces. To construct novel functional composites, we integrated metal complexes (*e.g.*, catalyst, photoreceptor, luminant, electron mediator, and molecular storage and separator) into the liposome space site-specifically. In the presentation, I will introduce the functionalization of liposome surface with lipophilic metal complexes such as the water oxidation catalyst<sup>(1)</sup> and the photoinduced release of nitric oxide<sup>(2)</sup>, and the ion-channel driven direct synthesis of coordination polymers in the inner aqueous phase.



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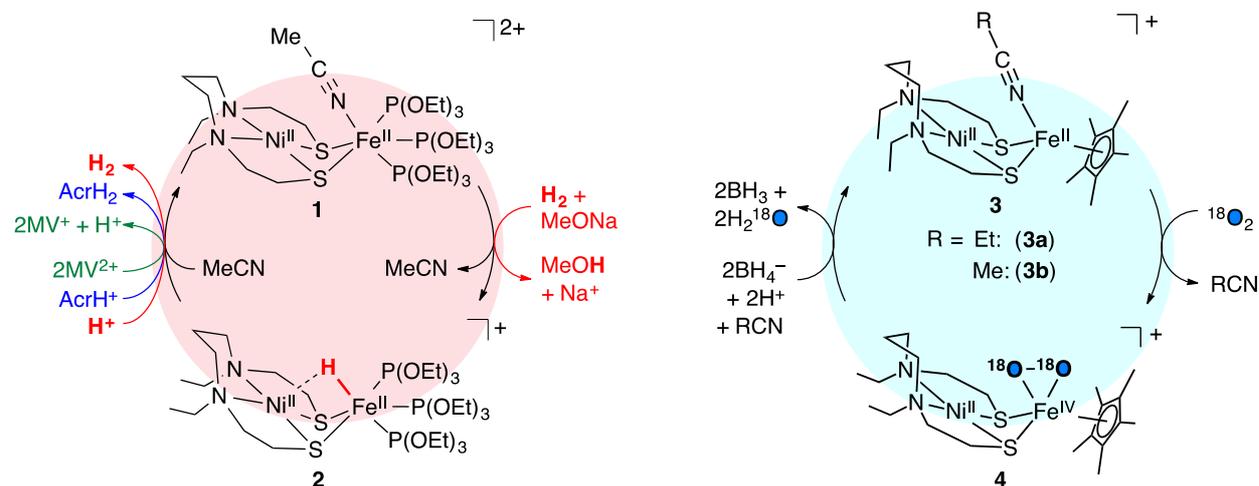
# H<sub>2</sub> and O<sub>2</sub> activation

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Hydrogen fuel cells generate electricity from the reaction between hydrogen and oxygen gas. Hydrogen power is expected to bring renewable energy to the forefront of energy generation. However, current fuel cells rely on rare and expensive platinum metal to make the reaction efficient, meaning they are usually too expensive for household applications. We have tackled this problem by replacing the platinum metal with molecular catalysts.<sup>1</sup> The advantage of molecular catalysts is that we can see exactly how they work. In 2011 we were the first to publish a working molecular catalyst for the hydrogen-splitting anode side of the fuel cell but this catalyst still needed expensive Ru.<sup>1,2,3</sup> The Fe-Ni hydrogen-splitting catalyst was reported in 2013.<sup>2</sup>

The oxygen-splitting catalyst is very similar to the hydrogen splitting catalyst, which is unusual for this kind of chemistry but not so surprising for us because natural hydrogenase enzymes can split both hydrogen and oxygen too. We are referring to enzymes found in bacteria from hot springs.<sup>3</sup> These enzymes are used by the bacteria to release electrons from hydrogen in nature and we have long been using them as a template for our designs. We knew natural hydrogenases could split both hydrogen and oxygen so we were sure we wouldn't have to modify our hydrogen catalyst too much to get oxygen splitting. In fact, we only had to exchange one set of electron-donating ligands for an even stronger ligand.<sup>3</sup> Nevertheless, the catalyst still had a surprise in store. The oxygen molecule binds side on to the Fe, which has a remarkably high +4 oxidation state. This is the first time such a structure has ever been isolated and we believe it gives a crucial new insight into the inner workings of natural hydrogenases and for the future development of fuel cell catalysts.<sup>4</sup>



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