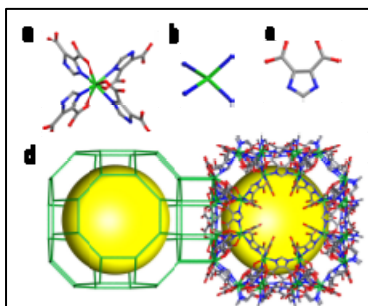


## Design, Synthesis, Functionalization, and Characterization of Metal-Organic Materials (MOMs) as:

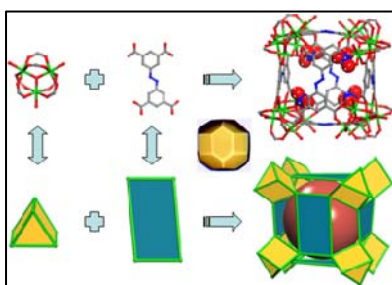
### Sustainable Energy Platforms:

- Utilize our single-metal-ion-based MBB approach, which involves judicious selection of the hetero-functional organic ligand to allow saturation of (6-8)-coordinate single-metal ions and the formation of rigid and directional building blocks  $[MN_{x+z}(CO_2)_{y+z}]$ ;  $x$  or  $y$  = individual coordination,  $z$  =  $N$ -member ring(s) of hetero-chelation,  $N = 5-6$ . This method is especially useful in the design and synthesis of zeolite-like metal-organic frameworks (ZMOFs), a subclass of MOMs that, like their inorganic analogues, lack interpenetration, possess accessible extra-large homogeneous openings and cavities, and have anionic frameworks.



**Figure 1.** The single-metal-ion-based MBB approach can be utilized to design and synthesize extra-large cavity ZMOFs. C = gray, O = red, N = blue, In = green; hydrogen atoms and guest molecules are omitted for clarity.

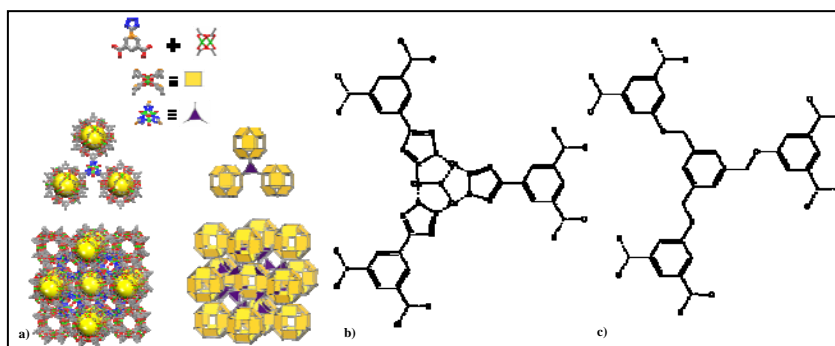
- Utilize metal-carboxylate-based MBBs, where multiple metal-oxygen  $[M_x(CO_2)_y]$  coordination bonds allow the generation of rigid nodes with fixed geometry, to design and synthesize porous, stable MOMs. Of particular interest for hydrogen and carbon dioxide storage are MOMs (e.g. *soc*-MOF) with narrower pores (<1 nm) and/or higher localized charge densities, which have been implicated in stronger interactions and higher uptakes at suitable temperatures and pressures.



**Figure 2.** The MBB approach can be utilized to design and synthesize targeted MOMs (e.g. *soc*-MOF) from metal-carboxylate clusters and polytopic carboxylate-based ligands. C = gray, O = red, N = blue, In = green; hydrogen atoms are omitted for clarity.

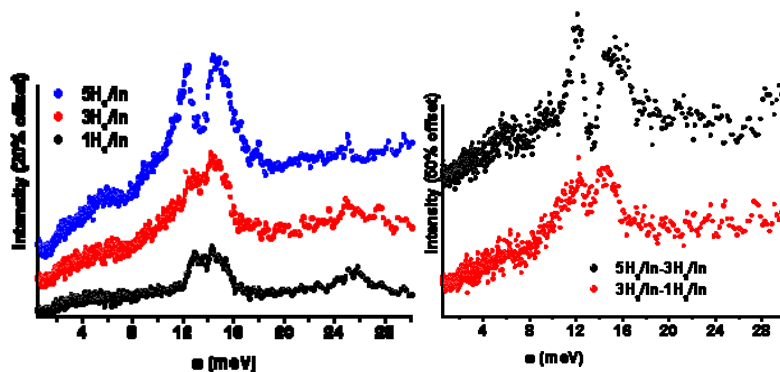
- Utilize supermolecular building blocks (SBBs), which involve enhanced built-in directional and structural information (e.g. high degree of symmetry and connectivity) compared to simple MBBs, as a rational route to the design and synthesis of porous MOMs with accessible extra-large cavities. We have utilized metal-organic polyhedra (MOPs, generated *in situ*), specifically metal-organic truncated cuboctahedra (generated *in situ*) that consist of 12 Cu-paddlewheel MBBs bridged by 24 5-tetrazolyl-1,3-benzendicarboxylate linkers (i.e. nanoballs), as 24-connected SBBs in the design and synthesis of a cationic *rht*-MOF with accessible large pores, including cavities in the mesoporous range. The uniqueness of the underlying *rht* network (i.e. it is the singular edge transitive net for the assembly of (3,24)-connected nodes) has allowed us to design

and synthesize a series of isorecticular MOFs with varied functionality, pore size/volume, and surface areas via expansion/functionalization the organic linkers.



**Figure 3.** a) The SBB approach can be utilized to design and synthesize extra-large cavity MOMs through b) coordinative or c) covalent cross-linking of MOPs. C = gray, O = red, N = blue, In = green; hydrogen atoms and guest molecules are omitted for clarity.

- Utilize inelastic neutron scattering (INS) to obtain a fundamental understanding of the interactions of sorbed  $H_2$  with both the organic and inorganic constituents of the porous framework of MOMs. One of the most prominent applications for which porous MOMs appear to have great potential is gas storage, especially hydrogen storage. MOM chemistry has introduced materials with some of the highest surface areas and hydrogen storage capacities for any porous material; however, the U. S. Department of Energy target(s) for hydrogen storage have not been met to date. In order to achieve these goals, an understanding of the hydrogen-MOF interactions is critical to the eventual design and synthesis of superior hydrogen storage materials. The most effective and sensitive method to study these interactions is INS, which allows the inference of specific hydrogen binding sites on the MOM. We have employed INS to study  $H_2$  sorption with respect to the strength of its interactions associated with binding sites in a variety of MOMs, including ZMOFs, *soc*-MOFs, and *rht*-MOFs.

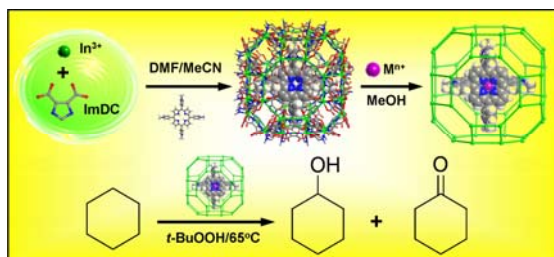


**Figure 4.** a) Inelastic neutron scattering spectra of *soc*-MOF obtained at 15 K for loadings of 1, 3, and 5  $H_2/In$ , and b) difference spectra. New peaks appearing at the highest loading become evident in the difference spectra in (b).

#### Catalytic Materials:

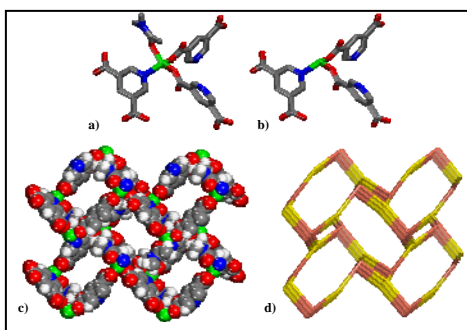
- ZMOFs can be synthesized from a variety of linkers and metals, and are readily tunable via ion exchange of small atoms/molecules and encapsulation of large molecules. Cationic single-metal ions/complexes, multi-metal clusters, and/or organic molecules that are of interest for various catalytic reactions and are smaller than the window dimensions can be exchanged, post-synthesis, for the as-synthesized extra-framework cations. The extra-large cavities of some ZMOFs also allow the *in situ* encapsulation of larger complexes, clusters, or molecules of interest for catalysis. We have successfully encapsulated cationic porphyrin molecules in the extra-large cages of one of our *rho*-

ZMOFs, as well as post-synthesis metallation of the porphyrin with Mn(II), which altogether showed catalytic activity toward the oxidation of cyclohexane.



**Figure 5.** The single-metal-ion-based MBB approach can be utilized to encapsulate large cationic porphyrin molecules in the extra-large cavities of *rho*-ZMOF. The porphyrin can then be metallated post-synthesis, which results in a system for catalysis of cyclohexane oxidation. C = gray, O = red, N = blue, In = green; hydrogen atoms and guest molecules are omitted for clarity.

- The single-metal-ion-based MBB approach is well-suited to the design and synthesis of MOMs with default topologies. Though a variety of architectures with varying connectivity are possible, 3-connected frameworks are of particular interest, because the default topology, *srs* [i.e. the Si net in SrSi<sub>2</sub> or (10,3)-*a*], is intrinsically chiral. Chiral MOMs have shown great promise in applications like nonlinear optics, asymmetric catalysis, and chiral separation; however, these applications typically require enantiopurity to be useful. Therefore, a logical design strategy to obtain not only chiral frameworks, but specifically homochiral MOMs is of great scientific interest. We have successfully implemented the single-metal-ion-based MBB approach to target *srs*-MOFs from the assembly of pre-designed 3-connected hetero-functional ligands, specifically 3,5-pyridinedicarboxylate, and 3-connected building units [MN<sub>x</sub>(CO<sub>2</sub>)<sub>y</sub>], generated *in situ*.

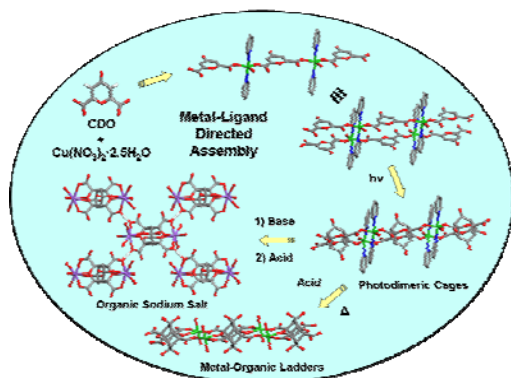


**Figure 6.** a) The single-metal-ion-based MBB, and b) the 3-connected BU of c) one *srs*-MOF, which can be simplified as having d) *srs* topology based on 3-connected nodes. [a-c) Carbon = gray, oxygen = red, nitrogen = blue, zinc = green; hydrogen atoms, terminal ligands, and guest molecules are omitted for clarity; d) ligand = yellow, M = orange.]

### Hybrid Metal-Organic/Bio-Materials:

- Aside from its rarity in MOFs and potential as a tritopic ligand (for generation of *srs*-MOFs), chelidonic (H<sub>2</sub>CDO) is interesting for a variety of reasons. H<sub>2</sub>CDO is a naturally occurring organic molecule found in a wide range of plant species, acting as a leaf-closing factor in some, and this biologically active molecule has been utilized in numerous applications, including skin-lightening and wound-healing ointments, anti-allergens, plant growth regulators, and cooking oil stabilizers, metal ion separations, and antibacterials. Several derivatives of H<sub>2</sub>CDO have been useful in other applications as well, making it a desirable ligand for incorporation into MOMs. In addition, H<sub>2</sub>CDO is a planar 4-pyrone-based molecule, i.e. a di-olefin, a factor that allows organic synthesis via [2+2] photodimerization (a cycloaddition reaction) of the carbon-carbon double bonds if they aligned nearly parallel and within 4.2 Å. Our metal-ligand directed assembly method has permitted the antiparallel positioning of pairs of CDO ligands within the required distance and exposure of the MOM crystals to UV light results in dual

cycloaddition of adjacent CDO ligands. The desired product, a photodimeric cage molecule, can be easily isolated for further studies. Similar tetraasterane-*like* compounds have exhibited interesting biological properties, most-notably anti-HIV and anti-cancer activities.



**Figure 7.** Chelidonic acid can be used as a ligand in MOMs. Metal-ligand directed assembly leads to proper positioning of the CDO for photodimerization, resulting in photodimeric cage molecules that can be isolated and/or used to synthesize new MOFs.