

## IV.I.3 Design and Synthesis of Novel Porous Metal-Organic Frameworks (MOFs) Toward High Hydrogen Storage Capacity

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### Statement of Objectives:

1. Synthesize viable porous MOFs for high H<sub>2</sub> storage at ambient conditions to be assessed by measuring H<sub>2</sub> uptake.
2. Develop a better understanding of the operative interactions of the sorbed H<sub>2</sub> with the organic and inorganic constituents of the sorbent MOF by means of inelastic neutron scattering (INS, to characterize the H<sub>2</sub>-MOF interactions) and computational studies (to interpret the data and predict novel materials suitable for high H<sub>2</sub> uptake at moderate temperatures and relatively low pressures).
3. Synergistically combine the outcomes of objectives 1 and 2 to construct a made-to-order inexpensive MOF that is suitable for super H<sub>2</sub> storage and meets the DOE targets.

The ongoing research is a collaborative experimental and computational effort focused on assessing H<sub>2</sub> storage and interactions with pre-selected metal-organic frameworks (MOFs) and zeolite-like MOFs (ZMOFs), with the eventual goal of synthesizing made-to-order high H<sub>2</sub> storage materials to achieve the DOE targets for mobile applications. We proposed in this funded research to increase the amount of H<sub>2</sub> uptake, as well as tune the interactions (i.e. isosteric heats of adsorption), by targeting readily tunable MOFs:

- 1)- Anionic open MOFs (i.e. ZMOFs) allow the addition of new sorption sites for H<sub>2</sub> in the void space (via post-synthesis modification aka ion exchange), an approach that is not feasible in neutral MOFs, and thus tunability of H<sub>2</sub> interactions by systematic evaluation of the extra-framework cations, a feature unique to anionic MOFs.

- 2)- Isorecticular compounds: a) allow the ability to easily modify the intra-framework constituents, assess their effect on H<sub>2</sub> sorption, and provide a direct comparison of the modified constituent(s) effects; our recently introduced *rht*-MOFs are excellent candidates for this method since *rht* is the only possible network for 3,24-connected nodes; b) permit systematic studies on the effect of pore volume on the amount of H<sub>2</sub> sorbed, since the ligands can be simply expanded while maintaining the same network topology.
- 3)- Model compounds can be used to assess the effect of pore size and functionality on H<sub>2</sub> sorption; molecular squares/boxes (MBs) are the systems of choice, because: a) they have been and can be synthesized from a variety of linkers (with myriad functionalities) and metals; b) to study the effects on H<sub>2</sub> sorption, their discrete nature and reduced unit cell (limited number of atoms) are ideally suited to molecular simulation studies; and c) the information gained from these MB systems can be implemented to design 3D MOFs (e.g. pillared 4.4 square grids, SGs) containing the desired attributes toward a material with strong H<sub>2</sub>-framework interactions, an attribute suitable for storing H<sub>2</sub> at room temperature and moderate pressures.

Accordingly, we divided our research objectives into five subgroups: 1) Anionic MOFs (ZMOFs serve as the exemplary platforms) allow the facile exchange of extra-framework cations, where the impact of charge and/or polarizability on the isosteric heats of adsorption can be assessed; several ZMOF platforms have been synthesized with various metals and ligands. 2) The isorecticular system provided by the 3,24-connected *rht*-MOFs allows tuning of inorganic and organic components and permits to evaluate the effects of functionalization, pore size, and pore volume for direct and systematic comparison in a similar class of networks. 3) Molecular boxes allow for simplified studies on the effect of pore size and functionalization on H<sub>2</sub> sorption energetics. 4) We can expand the MB approach to generate open pillared 3D structures with a combination of small windows, high surface area, and large volume for higher uptake at higher pressures. 5) Computational studies allow us to elucidate the impact of each component on the energetics of sorption and predict novel materials to be made. The collaborative effort has a final objective of the eventual design and synthesis of an advanced material for super H<sub>2</sub> storage.

## A. Description of Accomplishments

We have systematically investigated various strategies for substantial improvement of hydrogen binding energies in porous materials relative to those obtainable by simple physisorption in neutral MOFs or on carbons. This is being accomplished on several fronts, namely by the utilization of charged frameworks, reduction in pore size, tuning of pore geometries, incorporation of novel, open metal sites, and increases in the densities of the latter, as well as highly accurate and detailed computational studies on hydrogen interactions with porous hosts.

### A.1. Anionic MOFs

- Demonstrated the remarkable tunability (pores size, charge density, surface area) of anionic ZMOFs.
- Carried out the first successful ion exchange in a MOF (similarly to what is routinely done in zeolites) using the *rho*-ZMOF framework,  $[\text{Cation}^+_{48}][\text{In}_{48}(\text{C}_5\text{N}_2\text{O}_4\text{H}_2)_{96}]$ .
- Ions ( $\text{Li}^+$ ,  $\text{Mg}^{2+}$ ) exchanged were determined by single crystal X-ray diffraction to be hydrated and hydrogen-bonded to carboxylate oxygens, and are only indirectly accessible by  $\text{H}_2$ .
- Isothermic heats of adsorption for hydrogen approaching 9 kJ/mol are achieved in these materials due to their high charge density.
- Synthesized a metal organic material (ME737) with extremely large cavities by incorporation of more than one appropriate organic functionality (two bridging organic ligands, 2-amino-4,6-PmDc and oxalic acid) along with yttrium. This novel ZMOF has a zeolite topology, thus far only encountered in inorganic materials. The structure consists of cages with an internal diameter of 38 Å. Each cage consists of 144 yttrium metal centers, representing one of the most hierarchical complex MOMs reported to date.

### A.2. Effect of metal sites

- The effect of the intra-framework and extra-framework cations was investigated on the same platform namely sod-ZMOF.  $\text{H}_2$  binding energies varied from 8 to 8.4 kJ/mol depending on the cation.
- Successfully synthesized the Fe analog of In soc MOF, which exhibits enhanced isosteric heat of adsorption for hydrogen at the metal site from 6.5 to 7.5 kJ/mol. An analog of In soc MOF with the more highly polarizable Cl instead of water in the axial position exhibited a slight increase in binding strength for hydrogen near the In to 7.2 kJ/mol.
- Demonstrated enhanced binding energies (<9.5 kJ/mol) and high gravimetric capacity

(2.4 wt% at 78K ant 1 atm) in a unique compound  $[\text{Cu}_6\text{O}(\text{TZI})_3(\text{H}_2\text{O})_9(\text{NO}_3)]_n \cdot (\text{H}_2\text{O})_{15}$  of *rht* topology with a high density of open metal sites, which occur in two types of clusters. The *rht*-like network is suitable for achieving higher surface areas and larger free pore volumes (isoreticular chemistry).

### A.3. Effect of pore size; use of pillaring

- Reduction in pore size from 1.2 Å (PtS, topology) to 1.0 Å (Pth, topology) increases the average heat of adsorption for  $\text{H}_2$  by some 20%, along with a similar increase in gravimetric capacity.
- Development of three-dimensional frameworks from two-dimensional pillared structures for assessing the effect of pore size and geometry on hydrogen storage.
  - Reduction in the pore size by changing the pillar in  $\{\text{Zn}(\text{camphorate})(\text{bipy})_{0.5}\}_n$  from bipy (appr. 8x4 Å) to pyrazine (appr. 4x4 Å) increases the binding energy by 20% to more than 7 kJ/mol.

### A.4. Computational Studies

- Constructed the first highly accurate, transferable hydrogen potential energy function from high-level ab initio calculations at the MP4 level of theory using correlation-consistent methods. Includes accurate orientational dependence of the potential energy interactions with explicit polarization.
- Calculated adsorption isotherms for  $\text{H}_2$  in MOF-5 and soc MOF: show excellent agreement with experiment.
- Developed a supercomputing application, MPMC (Massively Parallel Monte Carlo) for sampling the Grand Canonical ensemble using techniques of statistical mechanical simulation.
- Demonstrated the effect of channel size on  $\text{H}_2$  interaction energies by building up box of benzene molecules. Inclusion of additional benzene rings to enclose a single  $\text{H}_2$  in an optimized box yields raises the interaction energies to near 13 kJ/mol from ~4 kJ/mol for a single benzene molecule.

## B. List of Papers

### Published

1. Nouar, F.; Eckert, J.; Eubank, J.F.; Forster, P.; Eddaoudi, M. "Zeolite-like Metal-Organic Frameworks (ZMOFs) as Hydrogen Storage Platform: Lithium and Magnesium Ion-Exchange and H-(rho-ZMOF) Interaction Studies" J. Am. Chem. Soc. 2009, 131, 2864-2870.
2. Liu, Y.; Kravtsov, V.; Eddaoudi, M. "Template-Directed Assembly of Zeolite-like Metal-Organic Frameworks

(ZMOFs): A usf-ZMOF with an Unprecedented Zeolite Topology” *Angew. Chem. Int. Ed.* 2008, 47(44), 8446-8449.

3. Nouar, F.; Eubank, J.F.; Bousquet, T.; Wojtas, L.; Zaworotko, M.; Eddaoudi, M. “Supermolecular Building Blocks (SBBs) for the Design and Synthesis of Highly Porous Metal-Organic Frameworks” *J. Am. Chem. Soc.* 2008, 130, 1833-1835.
4. Cairns, A.J.; Perman, J.; Wojtas, L.; Kravtsov, V.; Alkordi, M.; Eddaoudi, M.; Zaworotko, M. “Supermolecular Building Blocks and Crystal Design: 12-Connected Open Frameworks Based on a Molecular Cubohemioctahedron” *J. Am. Chem. Soc.* 2008, 130, 1560-1561.
5. Belof, J.L.; Stern, A.C.; Space, B. “An Accurate and Transferable Intermolecular Diatomic Hydrogen Potential for Condensed Phase Simulation” *J. Chem. Theory Comput.*, 2008 4(8), 1332-1337.
6. Belof, J.L.; Stern, A.C.; Eddaoudi, M.; Space, B. “On the Mechanism of Hydrogen Storage in a Metal-Organic Framework” *J. Am. Chem. Soc.* 2007, 129, 15202-15210.

#### Submitted

7. Sava, D.F.; Kravtsov, V. Ch.; Eubank, J.F.; Eckert, J.; Eddaoudi, M. “Exceptional stability and high hydrogen uptake in hydrogen bonded Metal-Organic Cubes (MOCs) possessing ACO and AST zeolite-like topologies” *J. Am. Chem. Soc.* 2009.

### C. List of People Working on the Project

In Year two, funds were requested in support of the equivalent of one full-time graduate student for each of three PIs located at USF, and one post-doctoral fellow. The following students were supported:

Student	type	months supported for the coverage dates of the present report
Amy Cairns	graduate	2.25
Dorina Sava	graduate	6.75
xFarid Nouar	graduate	4.50
John Perry	graduate	6.75
Jason Perman	graduate	2.25
Abraham Stern	graduate	4.50
John Belof	graduate	6.75
Dr. Xue Dong-Xu	post-doc	8.00