

## IV.C.1g A Biomimetic Approach to Metal-Organic Frameworks with High H<sub>2</sub> Uptake

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### Objectives

- Design, synthesis, and characterize metal-organic frameworks (MOFs) with active metal centers aligned in porous channels and accessible by H<sub>2</sub> molecules.
- Through optimized, cooperative binding, the MOFs are expected to have enhanced affinity to H<sub>2</sub>.
- These MOFs can help to reach the DOE 2010 and ultimately 2015 hydrogen storage goals.

### Technical Barriers

This project addresses the following technical barriers from the Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (P) Lack of Understanding of Hydrogen Physisorption and Chemisorption
- (Q) Reproducibility of Performance

### Technical Targets

- The focus of the proposed research is the use of concepts evident in metalloproteins to guide the synthesis of MOFs with gas-adsorption affinity around 15 to 20 kJ/mol for hydrogen.

- The overall objective is to achieve the DOE 2010 and 2015 system goals, primarily the gravimetric and volumetric storage goals, at or near ambient temperatures and moderate pressure for on-board vehicular hydrogen storage.

### Accomplishments

- Synthesized 30 new ligands for MOF formation.
- Optimized the open channel size and open-metal-center alignment in MOFs for hydrogen adsorption based on van der Waals interaction.
- Reached 12.5 kJ/mol hydrogen-adsorption heat.



### Introduction

In the field of hydrogen storage in MOFs, various strategies such as using pore size comparable to hydrogen molecules, increasing surface area and pore volume, utilizing catenation, and introducing coordinatively unsaturated metal centers (UMCs) have been widely explored to increase the hydrogen uptake of the MOFs. MOFs with hydrogen uptake approaching the DOE 2010 gravimetric storage goal under reasonable pressure but cryo-temperature (typically 77 K) were reported. However, the weak interaction between hydrogen molecules and MOFs has been the major hurdle limiting the hydrogen uptake of MOFs at ambient temperature.

### Approach

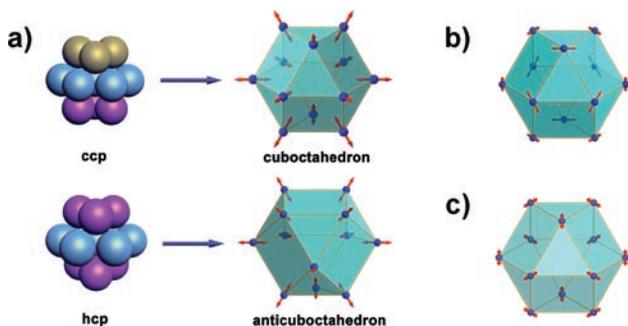
Our strategy to enhance H<sub>2</sub> uptake is to strengthen the MOF-H<sub>2</sub> interaction by increasing the number of nearest neighboring open-metal-sites of each H<sub>2</sub>-hosting void in a 3-dimensional (3D) framework and to align the open-metal-sites so that they can interact directly with the guests (H<sub>2</sub> molecules) inside the void.

In close-packing of spheres, such as cubic close-packing (ccp) or hexagonal close-packing (hcp), each sphere has a maximum of 12 nearest neighbors. Connecting the 12 neighbors gives rise to a cuboctahedron for ccp or an anticuboctahedron for hcp. If the central sphere is removed and the void left is used for H<sub>2</sub>-hosting, the MOF-H<sub>2</sub> interaction can be strengthened by placing open-metal-sites at the 12 corners of a cuboctahedron or anticuboctahedron (Figure 1).

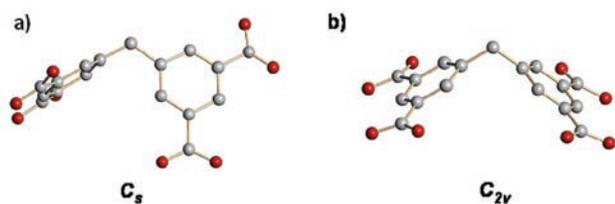
## Results

By using isophthalate and a dimetal paddlewheel structural motif, a cuboctahedral cage or an anticuboctahedral cage can be prepared. If the isophthalate motif is extended at the 5 position using another moiety that contains one or more carboxylate groups, the polyhedron can be extended into a cuboctahedral or anticuboctahedral framework, which should have high hydrogen uptake. Although quite a few MOFs with appreciable hydrogen uptake have been intuitively constructed this way, the open-metal sites in these MOFs are often misaligned due to the geometric constraints of the ligands, preventing the further enhancement of the MOF- $H_2$  interaction (Figures 1b and 1c).

A possible design for an “ideal” ligand for the construction of a MOF based on cuboctahedral cages with aligned open-metal-sites is to keep the two isophthalate moieties to ensure the formation of the cuboctahedral cages but link the two using a *bent* bridge to prevent the formation of an NbO type structure. The ligand designed using such a strategy is 5,5'-methylene-di-isophthalate (mdip, Figure 2). Herein we report two Cu-mdip MOFs that are polymorphs of each other: a MOF consisting of cuboctahedra with all open-metal-



**FIGURE 1.** a) Two common types of close-packing of spheres and their corresponding polyhedra; the red arrows demonstrate the ideal placement of open-coordination sites of paddlewheel dimetal units; b) One cuboctahedron drawn with atomic coordinates retrieved from the crystal data of HKUST-1; c) Cuboctahedron drawn using atomic coordinates from the crystal data of MOF-505 with an emblematic NbO type topology.



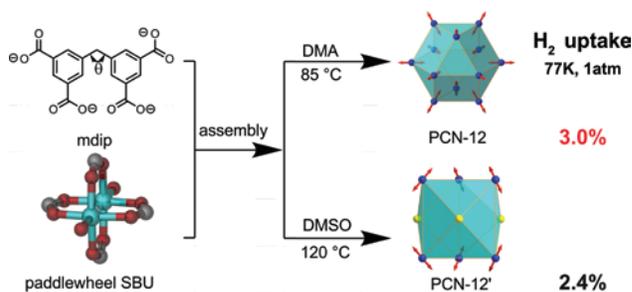
**FIGURE 2.** Two extreme conformations of 5,5'-methylene-di-isophthalate (mdip).

sites aligned, porous coordination network (PCN)-12, and PCN-12', in which the open-metal-sites are out of alignment, as the basis for comparison (Figure 3).

The reason that polymorphism arises in Cu-mdip MOFs is due to the two extreme conformations of mdip: a form with  $C_s$  point group symmetry, in which the two benzene rings of mdip are perpendicular to each other (Figure 2a); and a  $C_{2v}$  form that can be generated by symmetry with one-fourth of the ligand (Figure 2b). PCN-12 exhibits a record-high hydrogen uptake of 3.05 wt% at 77 K and 1 bar for a MOF, in contrast to an uptake of 2.40 wt% for PCN-12' under the same condition. The remarkable difference of hydrogen uptake of the two MOF reflects the dissimilar open-metal-site alignments in the two polymorphs (Figure 3). The heat of adsorption of hydrogen for PCN-12' is 7.13 kJ/mol, but that of PCN-12 can reach as high as 12.5 kJ/mol at low coverage. To the best of our knowledge, PCN-12 possesses so far the highest hydrogen uptake and the highest heat of  $H_2$ -adsorption among those of reported MOFs under 77 K and 1 bar.

To evaluate high-pressure hydrogen sorption properties of PCN-12 and PCN-12', hydrogen isotherms were measured in the pressure range of 0-50 bar at 77 K and 298 K. At 50 bar and 77 K, the excess volumetric (gravimetric) adsorption in PCN-12' is 23.6 g/L (2.58 wt%). Consistent with the trend shown in the low-pressure adsorption studies, the excess volumetric (gravimetric) adsorption of PCN-12 is as high as 45.7 g/L (5.61 wt%). This remarkable volumetric hydrogen uptake, though at cryo-temperature, compares favorably to the 2010 DOE target of 45 g/L. The hydrogen adsorption curve of PCN-12 is not saturated and the uptake may still increase if the pressure increases. In contrast, the hydrogen adsorption curve for PCN-12' at 77 K is almost saturated at less than 12 bar. The relatively high volumetric storage density can be attributed to the higher density of PCN-12 compared to super-light MOFs such as MOF-5 and MOF-177.

For practical applications, the total hydrogen uptake defined as the total amount of hydrogen stored in the



**FIGURE 3.** The synthesis, open-metal-site alignment, and hydrogen uptake of the two MOF polymorphs: PCN-12 and PCN-12'.

bulk volume of the materials can usually provide another informative quantity, though the mass and volume of a storage tank may need to be considered when the “system goal” is concerned.

The total H<sub>2</sub> adsorption was calculated by using the method reported for other MOFs. Skeletal densities of 3.47 g/cm<sup>3</sup> and 2.71 g/cm<sup>3</sup> for PCN-12 and PCN-12', respectively, were used to determine the total amount of H<sub>2</sub> adsorption under isothermal conditions. These skeletal density data were derived from pore volumes of 0.94 cm<sup>3</sup>/g (PCN-12) and 0.72 cm<sup>3</sup>/g (PCN-12') measured experimentally from N<sub>2</sub> isotherms at 77 K and crystal densities of 0.814 g/cm<sup>3</sup> (PCN-12) and 0.910 g/cm<sup>3</sup> (PCN-12) obtained from single-crystal X-ray data. The total gravimetric hydrogen uptake of PCN-12' is just 3.85 wt% at 77 K and 50 bar, corresponding to a total volumetric uptake of 35.3 g/L. In contrast, the total gravimetric hydrogen uptake of PCN-12 is 7.12 wt%, corresponding to a total volumetric value of 58.0 g/L. PCN-12 represents one of very few MOFs with their gravimetric and volumetric hydrogen uptakes comparable to the 2010 DOE targets (6.0 wt% and 45 g/L), albeit at 77 K and the DOE targets are “system goals”.

## Conclusions and Future Directions

### Conclusions

- MOFs containing UMCs or entatic metal centers tend to have high hydrogen affinity.
- MOFs containing well-aligned UMCs possess high heat of hydrogen adsorption.
- MOFs constructed based on close-packing patterns have high hydrogen uptake.
- Nanoscopic cages such as cuboctahedral cages are particularly suitable for hydrogen storage.

### Future Directions

- Further enhancement of H<sub>2</sub>-MOF interaction by the introduction of higher density of coordinatively unsaturated metal centers (heat of adsorption 15 kJ/mol).
- Improvement of H<sub>2</sub> uptake at temperatures higher than 77 K by ligand and MOF design.
- Increase MOF thermal stability while maintaining its porosity.
- Preparation of MOFs with high surface area and optimized cage size (4,500 m<sup>2</sup>/g).
- Improve the usable storage capacity of MOFs.

## FY 2008 Publications/Presentations

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2. “Hydrogen Adsorption in a Highly Stable Porous Rare-Earth Metal–Organic Framework: Sorption Properties and Neutron Diffraction Studies” J. Luo, H. Xu, Y. Liu, Y. Zhao, L.L. Daemen, C. Brown, T.V. Timofeeva, S. Ma, and H.-C. Zhou. *J. Am. Chem. Soc.*, 2008, *130*, 9626.
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5. “Metal-organic frameworks based on double-bond-coupled di-isophthalate linkers with high hydrogen and methane uptakes.” X.-S. Wang, S. Ma, K. Rauch, J.M. Simmons, D. Yuan, T. Yildirim, W.C. Cole, J.J. Lopez, A. De Meijere, and H.-C. Zhou. *Chem. Mater.*, 2008, *20*, 3145.
6. “Nano/microporous materials: Hydrogen storage materials.” D.J. Collins and H.-C. Zhou. In *Nanomaterials: Inorganic and Bioinorganic Perspectives*; C.M. Lukehart and R.A. Scott, Eds.; Wiley: New York, 2008, *in press*.
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9. “Metal-organic framework based on a trinickel secondary building unit exhibiting gas-adsorption hysteresis.” S. Ma, X.-S. Wang, E.S. Manis, C.D. Collier, and H.-C. Zhou. *Inorg. Chem.*, 2007, *46*, 3432.
10. “Hydrogen storage in metal-organic frameworks.” D.J. Collins and H.-C. Zhou, *J. Mater. Chem.*, 2007, *17*, 3154.
11. “A mesh-adjustable molecular sieve for general use in gas separation.” S. Ma, D. Sun, X.-S. Wang, and H.-C. Zhou, *Angew. Chem. Int. Ed.*, 2007, *46*, 2458.
12. “Framework-catenation isomerism in metal-organic frameworks and its impact on hydrogen uptake.” S. Ma, D. Sun, M. Ambrogio, J.A. Fillinger, S. Parkin, and H.-C. Zhou, *J. Am. Chem. Soc.*, 2007, *129*, 1858.