

IV.C.1 A Biomimetic Approach to Metal-Organic Frameworks with High H₂ Uptake

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Fiscal Year (FY) 2012 Objectives

- Design, synthesis, and characterization of metal-organic frameworks (MOFs) with potential anchors for active metal centers introduction.
- Design, synthesis, and optimization of porous polymer frameworks (PPNs) with different functionalities.
- These functionalized MOFs and PPNs demonstrate much enhanced H₂ affinity through optimized, cooperative binding. The results can be a great help in designing advanced porous materials to reach the DOE 2010 and ultimately 2017 hydrogen storage goal.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Fuel Cell 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 2017 system goals, primarily the gravimetric and volumetric storage goals, at or near-ambient temperatures and moderate pressure for onboard vehicular hydrogen storage (Table 1).

TABLE 1. Technical System Targets: Onboard Hydrogen Storage for Light-Duty Vehicles

Storage Parameter	Units	2010	2017	Ultimate
System Gravimetric Capacity: Usable, specific-energy from H ₂ (net useful energy/max system mass)	kWh/kg (kg H ₂ /kg system)	1.5 (0.045)	1.8 (0.055)	2.5 (0.075)
System Volumetric Capacity: Usable energy density from H ₂ (net useful energy/max system volume)	kWh/L (kg H ₂ /L system)	0.9 (0.028)	1.3 (0.040)	2.3 (0.070)

FY 2012 Accomplishments

- High-surface-area MOFs (PCN-82 and PCN-88) with potential anchors for metal incorporation were synthesized, the calculated heat of adsorption for PCN-82 is 6.6 kJ/mol at zero loading, and this value compares favorably with MOFs lacking special sorption sites.
- Highly stable Zr-MOF with metalloporphyrin ligand (PCN-223) was synthesized and initial metal-insertion study was carried out, these materials exhibit high surface area and high heat of adsorption for H₂.
- Low-cost PPN enriched with phenol groups (PPN-43) was synthesized, phenol group can be served as anchor for metal incorporation, therefore high heat of adsorption for H₂.
- A series of biphenyl ring PPNs have been designed and synthesized, these materials are relatively low cost, but exhibit high surface areas and high heats of adsorption for H₂.



Introduction

In the past decade, there has been an escalation of interest in the study of MOFs due to their fascinating structures and intriguing application potential. Their exceptionally high surface areas, uniform yet tunable pore sizes, and well-defined adsorbate-MOF interaction sites

make them suitable for hydrogen storage. Various strategies to increase the hydrogen capacity of MOFs, 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. Recently, inelastic neutron scattering and neutron powder diffraction as well as computational studies suggest that the choice of both metal centers and ligands can play an important role in tailoring the gas-framework interactions. Additionally, those ligands containing phenyl rings have been proved favorable for hydrogen desorption. 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 H₂ uptake was as follows:

- (1) prepared the catenation isomer pair to evaluate the contribution from catenation to the hydrogen uptake of a MOF material. Catenation can be utilized to reduce pore sizes in porous MOFs and has also been explored as an efficient method to improve the hydrogen uptake of MOFs.
- (2) Synthesized porous MOFs with high hydrogen adsorption capacities based on different coordinatively UMCs. The implementation of coordinatively UMCs into porous MOFs has been considered one of the most attractive ways to improve their affinities to hydrogen.
- (3) Hydrogen storage studies in MOFs containing nanoscopic cages based on double-bond-coupled di-isophthalate linkers. Those ligands containing phenyl rings in MOFs have been proved favorable for hydrogen adsorption.
- (4) Design and synthesize porous MOFs based on an anthracene derivative which can provide additional hydrogen binding sites to increase the hydrogen uptake.
- (5) Obtained stable MOFs with high surface areas by the incorporation of mesocavities and microwindows.
- (6) Constructed MOFs with “close-packing” alignment of open metal sites, which can increase the number of nearest neighboring open metal sites of each H₂-hosting void in a three-dimensional (3-D) framework so that they can interact directly with the guests (H₂ molecules) inside the void.
- (7) Built up porous lanthanide MOFs and studied their potential application in gas adsorption.
- (8) Prepared an unprecedented linkage isomer pair of MOFs and studied the impact of pore size on H₂ storage capacity in MOFs.
- (9) Incorporated polyynes unit into MOFs, which has higher H₂ affinity.
- (10) Construct stable and high-surface-area Zr-MOFs, study the effect on gas uptake by introducing different metals into their porphyrin linkers.
- (11) Design and synthesize PPNs with high chemical stability suitable for further

decoration. (12) Incorporated metal ions into PPNs, which can enhance the isosteric heats of hydrogen-adsorption.

Results

In the past year, we have prepared a series of MOFs and PPNs and explored their potential applications in hydrogen storage. Table 2 shows the comparison of hydrogen heat of adsorption, uptake at low pressure, and Brunauer-Emmett-Teller (BET) surface area of selected MOFs and PPNs. Next we will discuss in detail the results of H₂ uptakes of these materials.

TABLE 2. Comparison of Hydrogen Heat of Adsorption, Uptake at Low Pressure, and BET Surface Area of Selected MOFs and PPNs

Material	ΔH_{ads} (kJ/mol)	Uptake at 77 K and 1 bar (wt%)	BET surface area (m ² /g)
PCN-82	6.6	2.7	4,488
PCN-88	6.0	2.6	3,300
PCN-223-Zr; -Fe; -Ni	8.7; 8.0; 8.5	1.6; 1.5; 1.2	2,200 (Fe)
PPN-43	8.6	1.2	1,040
PPN-10	8.4	1.0	1,128
PPN-12	5.8	1.7	3,420
PPN-13	8.2	1.4	1,026
PPN-14; 15; 16	7.1; 7.9; 8.7	1.6; 1.2; 1.2	1,910; 873; 794

a. High-surface-area MOF (PCN-88) with pre-designed single-molecule trap (SMT) for pyrazine derivatives

A newly designed tetratopic carboxylic acid ligand 5,5'-(naphthalene-2,7-diyl)diisophthalic acid (H₄L) was synthesized by Pd-catalyzed coupling reactions between 2,7-dibromonaphthalene and diethyl 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)isophthalate. H₄L reacted with Cu(NO₃)₂·2.5H₂O under solvothermal conditions affording PCN-88, which has a 3-D framework structure containing the pre-designed SMT units (Figure 1a).

After activation at 100°C under reduced pressure, PCN-88 retained its crystallinity as confirmed by powder X-ray diffraction (PXRD). The N₂ and Ar adsorption isotherms at 77 and 87 K further revealed its permanent porosity. A two-step adsorption was observed in N₂ and Ar isotherms, with BET and Langmuir surface areas of 3,308 and 3,845 m²/g, respectively.

In the low pressure region, the hydrogen-uptake capacity is largely controlled by the hydrogen affinity towards the framework, which can be quantified by heat of adsorption. Variable-temperature measurements reveal an isosteric heat of adsorption of 6.0 kJ/mol for PCN-88 at zero loading, as a result, PCN-88 can take up a remarkable 320 cm³/g (2.7 wt%) of H₂ at 77 K and 1 bar (Figure 1b). The value is among the highest of reported porous materials at low pressure. Work is

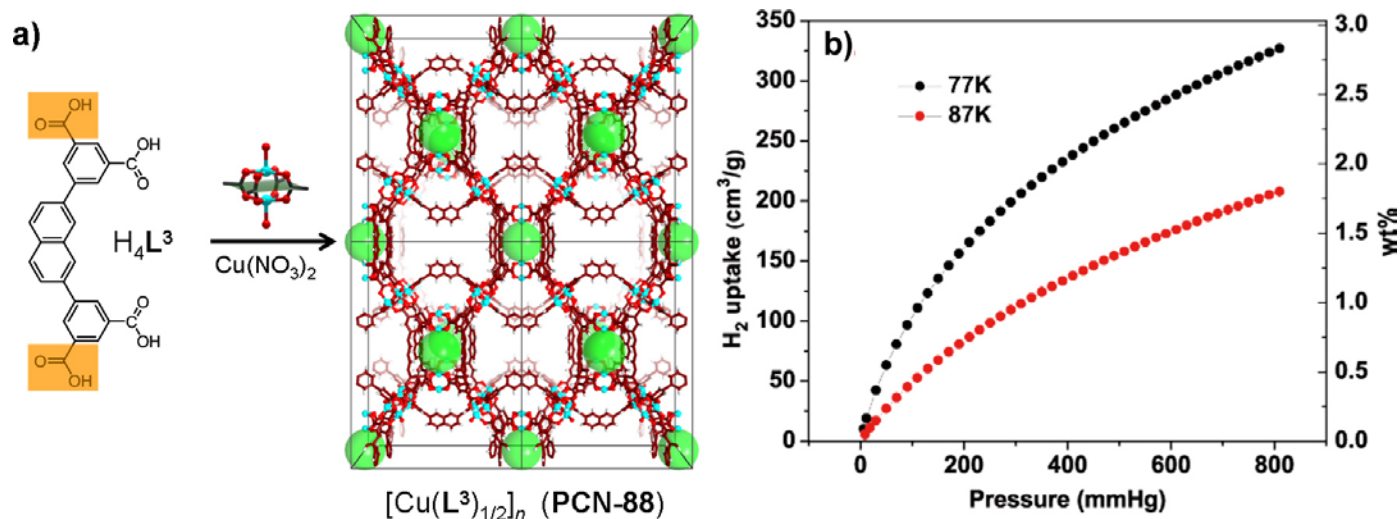


FIGURE 1. (a) Schematic representation of the construction of PCN-88 and its 3-D framework structure. (b) Low-pressure hydrogen isotherms of PCN-88 at 77 and 87 K.

continuing on introducing pyrazine derivatives into SMT and their heats adsorption for H_2 .

b. Highly porous MOF sustained with 12-connected nanoscopic octahedra

The tetra-carboxylate ligand, bpbcd, with a 90° -angle-carbazole-3,6-dicarboxylate moiety as opposed to the widely used 120° -angle-isophthalate, was synthesized by a Cu(I)-catalyzed reaction between dimethyl 9H-carbazole-3,6-dicarboxylate and 1,4-dibromo-2,5-dimethoxybenzene followed by hydrolysis. Solvothermal reaction of H_4 bpbcd and $Cu(NO_3)_2 \cdot 2.5H_2O$ in the presence of HBF_4 afforded green block crystals PCN-82 (Figure 2a).

The N_2 sorption for freeze-dried PCN-82 at 77 K exhibited a reversible Type-I isotherm as shown in Figure 2b, a characteristic of microporous materials. PCN-82 exhibits exceptionally high N_2 uptake (ca. $1,100 \text{ cm}^3/g$). By applying the BET model (up to $P/P_0 \approx 0.05$), the apparent surface area is estimated to be $\sim 4,488 \text{ m}^2/g$ (calculated $\sim 4,307 \text{ m}^2/g$) and Langmuir surface area $\sim 4,859 \text{ m}^2/g$, which is similar to MOF-177 (BET $\sim 4,500 \text{ m}^2/g$).

Variable-temperature measurements reveal an isosteric heat of adsorption of 6.6 kJ/mol for PCN-82 at zero loading, this value compares favorably with MOFs lacking special sorption sites; their heats of adsorption are typically in the $4\text{--}5 \text{ kJ/mol}$. The excellent performance of PCN-82 can be attributed to the availability of open metal sites, microporous nature and exceptionally high surface area, as a result, PCN-82 can take up a remarkable $300 \text{ cm}^3/g$ ($2.6 \text{ wt}\%$) of H_2 at 77 K and 1 bar (Figure 2c). Work is ongoing to introduce different functionalities onto benzene linkers to improve their heat adsorption for H_2 .

c. Highly stable mesoporous zirconium MOFs with metalloporphyrin ligand

Solvothermal reactions of metalloporphyrin M-TCPP (TCPP = tetrakis(4-carboxyphenyl)porphyrin, $M = Fe, Mn, Co, Ni, Cu, Zn, H_2$), $ZrCl_4$ and benzoic acid yielded needle shaped single crystals of PCN-223. Different from the well-known 12-connected Zr_6 cluster observed in the UiO-series of MOFs, only eight edges of the Zr_6 octahedron are bridged by carboxylates from TCPP ligands in PCN-223, while the remaining positions are occupied by terminal $-OH$ groups (Figure 3a).

The porosity of PCN-223 has been examined by nitrogen adsorption experiments at 77 K. The typical type IV isotherm of PCN-223(Fe) exhibits a steep increase at the point of $P/P_0 = 0.3$, suggesting meso-porosity. A N_2 uptake of $1,009 \text{ cm}^3/g$ and a BET surface area of $2,200 \text{ m}^2/g$ have been observed for PCN-223(Fe), the pore volume of $1.56 \text{ cm}^3/g$ is also in good agreement with the calculated pore volume of $1.63 \text{ cm}^3/g$. Other PCN-223 MOFs with different porphyrin centers also displayed similar type IV N_2 sorption isotherms and gave surface area, N_2 uptake, and total pore volume up to $2,312 \text{ m}^2/g$, $1,067 \text{ cm}^3/g$, and $1.65 \text{ cm}^3/g$, respectively.

The PXRD patterns remain intact upon immersion in water, boiling water, as well as 2M, 4M, 8M, and even concentrated hydrochloric acid (HCl) aqueous solutions for 24 h, suggesting no phase transition or framework collapse happening during these treatments (Figure 3b). More importantly, the N_2 sorption isotherms remained almost the same upon all treatments, which further confirmed the intactness of the tested frameworks. Strikingly, PCN-223(Fe) survived even after the treatment with concentrated HCl,

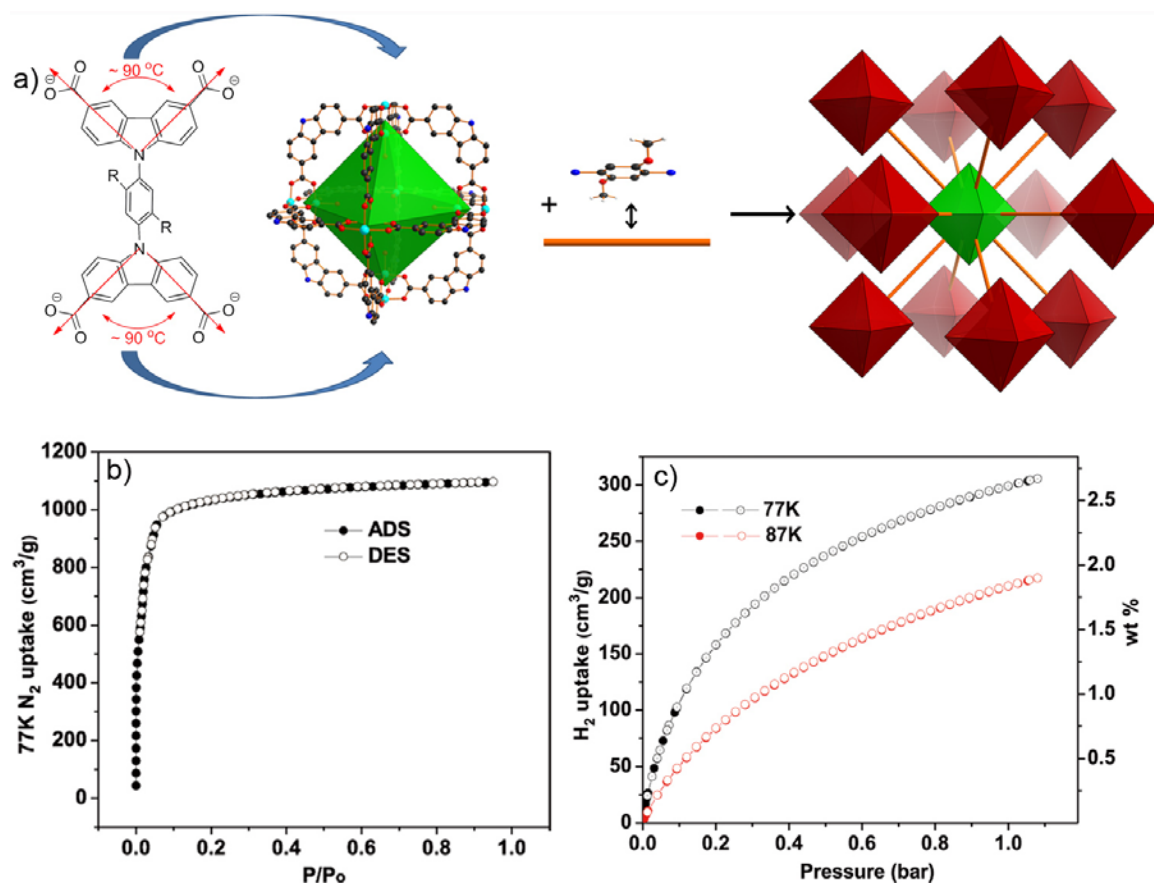


FIGURE 2. (a) Schematic representation of the construction of PCN-82 and its 3-D framework structure. (b) 77 K N₂ isotherm for PCN-82. (c) Low-pressure hydrogen isotherms of PCN-82 at 77 and 87 K.

a strong acid, which has rarely been observed for MOF materials, showing its exceptionally high chemical stability.

Variable-temperature measurements reveal isosteric heats of adsorption of 8.7, 8.0, and 8.5 kJ/mol for PCN-223(Zr), PCN-223(Fe), and PCN-223(Ni), respectively, at zero loading (Figure 3c, 3d). The high value can be partially attributed to the incorporated metal centers in the porphyrin ligand.

d. Functionalized PPN design and synthesis

The advantages of phenolic resin are high density of phenol, high stability, easy to scale up, et al. These properties are extremely important for practical gas storage applications. To render these properties into porous polymers, we designed and synthesized a tetrahedral polyphenol 4,4',4'',4'''-methanetetrayltetraphenol. With this tetrahedral monomer reacted with formaldehyde, we successfully synthesized a PPN-43 with remarkable density of phenol group. PPN-43 exhibits BET surface area as high as 1,040 m²/g, by measuring H₂ uptake at various temperatures, H₂ heat of adsorption for PPN-43 was calculated to be 8.6 kJ/mol at zero loading.

Considering its superb physiochemical property, our group is working on optimizing reaction conditions to further improve the surface area; and the study of using phenol group as an anchor for multivalent metals incorporation is also underway.

Oxidative Eglinton coupling of terminal alkynes has been proven very efficient in polymerization reactions. We designed and synthesized a series of biphenyl ring tetrahedral monomers, the two phenyl rings are in a perpendicular position by the substitution at 2,2',6,6' positions. We successfully synthesized a series of PPNs, among them; PPN-12 shows a BET surface area as high as 3,420 m²/g (Figure 4a). PPN-13 with all fluorine substitution has the highest heat of adsorption for H₂. We also tried to release the phenol groups in PPN-14, and convert it into phenolic lithium (Figure 4b). Although surface area significantly decreased with this procedure, the increase of heat of adsorption is obvious (Figure 4d). Work is continuing in our group to optimize the reactions and incorporate other functionalities to further improve heat of adsorption.

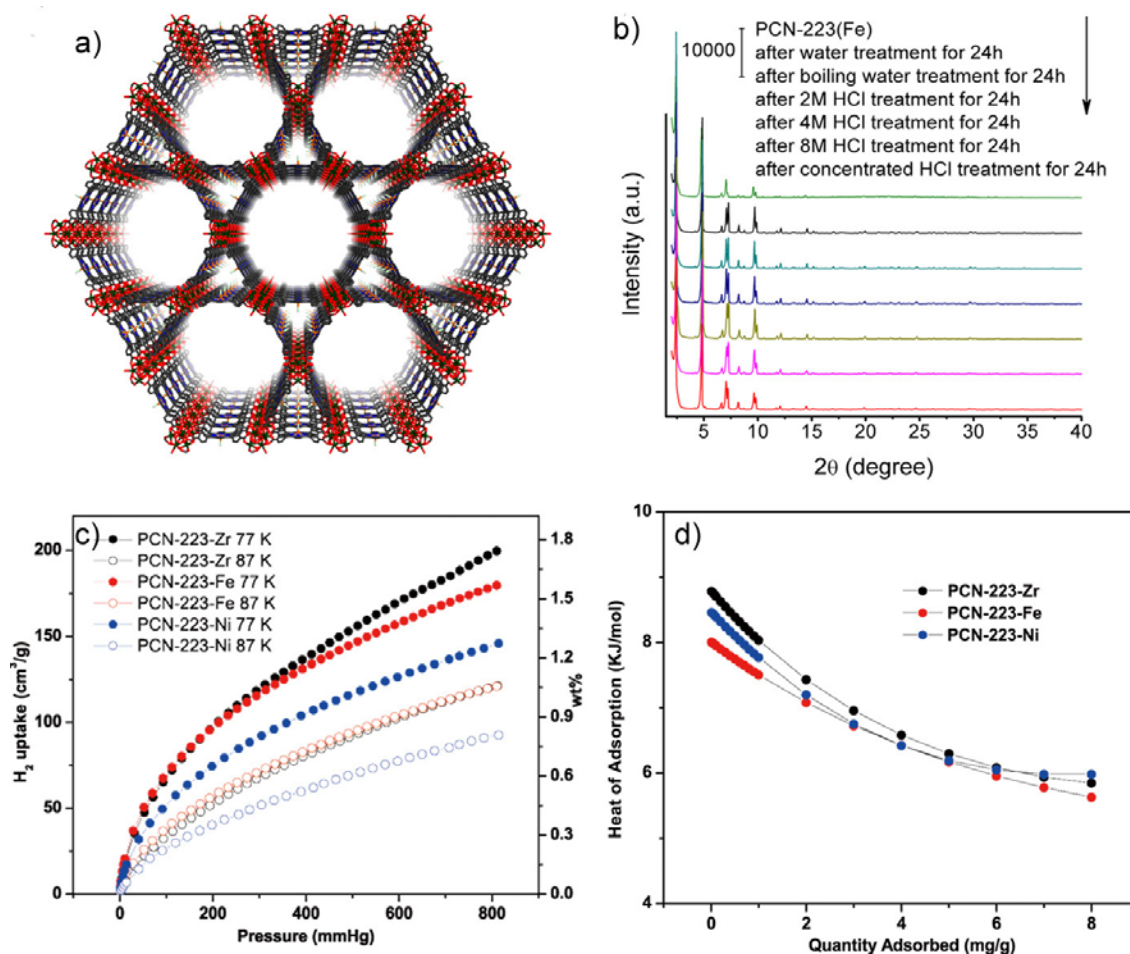


FIGURE 3. (a) Crystal structure and underlying network topology of PCN-223(Fe). (b) Powder X-ray diffraction pattern upon treatments with water, boiling water, 2M, 4M, 8M and even concentrated HCl. (c) Low-pressure hydrogen isotherms of PCN-223 at 77 and 87 K. (d) Calculated heats of adsorption of PCN-223.

Conclusions and Future Directions

Conclusions:

- Two MOFs (PCN-82 and PCN-88) with exceptionally high surface areas (4,488 and 3,300 m²/g) have been designed and synthesized. They all have high heat of adsorption and potential anchors for metal incorporation.
- A series of high-surface-area Zr-MOFs were synthesized by using metalloporphyrin ligands, these MOFs are stable even in strong acidic conditions. Initial study shows that metal incorporation leads to high heat of adsorption for H₂.
- A phenolic PPN was synthesized, the phenol group can serve as an anchor for multivalent metal incorporation.
- A series of biphenyl PPNs were designed and synthesized by using triple bond coupling reaction, the biphenyl ring is “locked” by introducing functional groups at 2 & 2' positions, therefore leading to high-surface-area PPNs, and high heat of adsorption for H₂.

Future Directions:

- Further enhancement of H₂-MOF interaction by doping coordinatively unsaturated metal centers (heat of adsorption 15 kJ mol⁻¹). Based on theoretical calculations, main group metals such as Li, Mg and Ca and multivalent metals, such as V³⁺, Fe³⁺, Ti³⁺, etc. will be tested.
- Working with partners, test H₂ uptake at temperatures higher than 77 K.
- Preparation of MOFs with high surface area and optimized cage size with newly designed ligands based on theoretical calculations.
- Incorporation of entatic-state metals based on theoretical guidance.
- Preparation of new PPNs containing active metals.

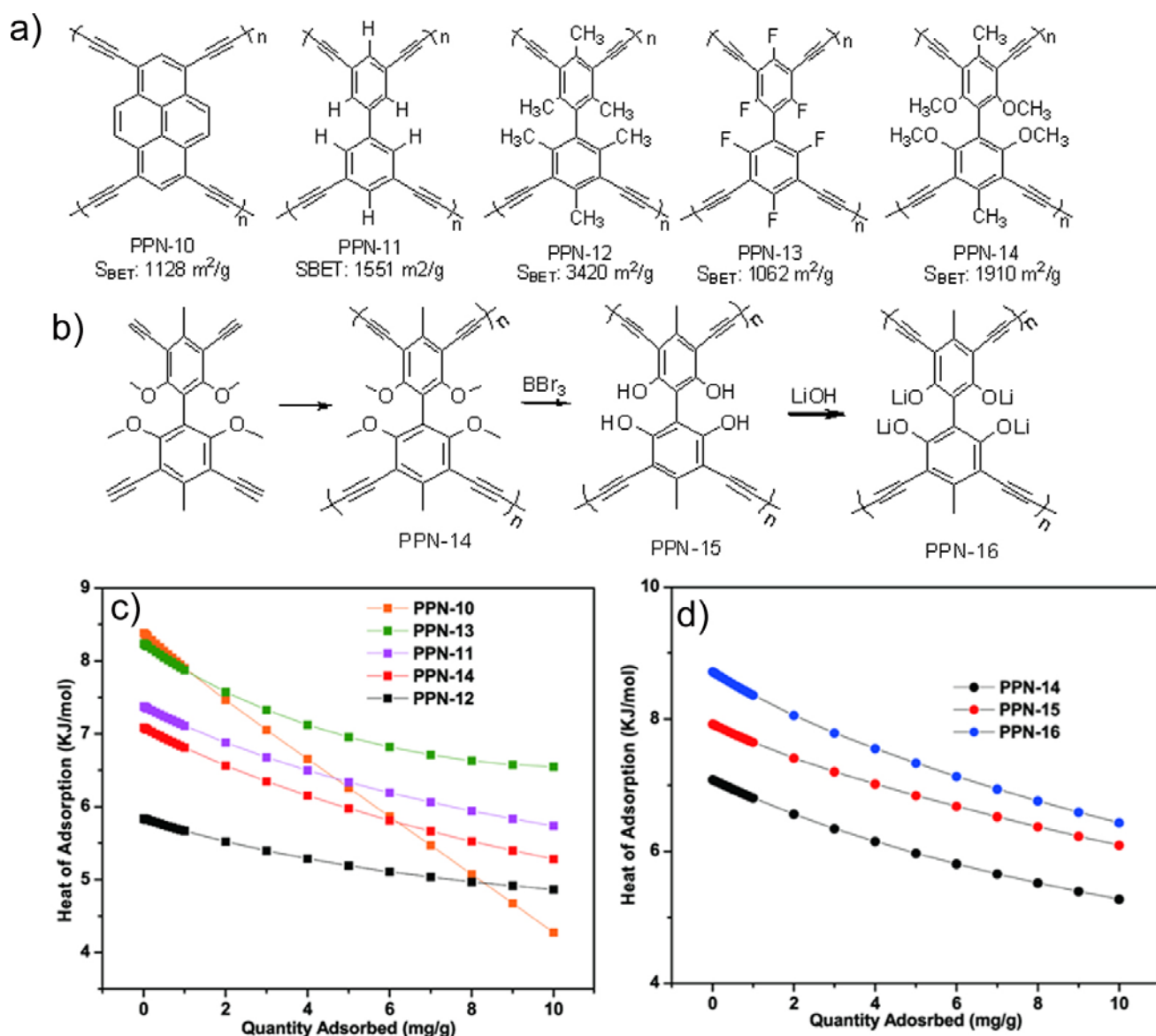


FIGURE 4. (a) The structure of biphenyl ring PPNs with their calculated BET surface areas. (b) Synthetic scheme of PPN-15 and 16. (c) The calculated H_2 heats of adsorption for PPN-10, 11, 12, 13, and 14. (d) The calculated H_2 heats of adsorption for PPN-14, 15, and 16.

FY 2012 Publications/Presentations

Publications

- “Highly Stable Porous Polymer Networks with Exceptionally High Gas-Uptake Capacities”, Yuan, D.; Lu, W.; Zhao, D.; Zhou, H.-C., *Adv. Mater.* **2011**, *23*, 3723–3725.
- “Sulfonate-Grafted Porous Polymer Networks for Preferential CO_2 Adsorption at Low Pressure”, Lu W.; Yuan D.; Sculley J.; Zhao D.; Krishna R.; Zhou, H.-C., *J. Am. Chem. Soc.* **2011**, *133* (45), 18126–18129.
- “Isomerism in Metal-Organic Frameworks: “Framework Isomers”, Makal, T. A.; Yakovenko, A.; Zhou, H.-C., *J. Phys. Chem. Lett.*, **2011**, *2*, 1682–1689.

- “A Robust Metal-Organic Framework with An Octatopic Ligand for Gas Adsorption and Separation: A Combined Characterization by Experiments and Molecular Simulations”, Zhuang, W.; Yuan, D.; Liu, D.; Zhong, C.; Li, J.-R.; Zhou, H.-C., *Chemistry of Materials*, **2011**, *24* (1), 18–25.
- “Pressure-Responsive Curvature Change of a “Rigid” Geodesic Ligand in a (3,24)-Connected Mesoporous Metal-Organic Framework”, Yuan, D.; Zhao, D.; Zhou, H.-C., *Inorg. Chem.* **2011**, *50* (21), 10528–10530.
- “A Porous Metal-Organic Framework with Helical Chain Building Units Exhibiting Facile Transition from Micro- to Mesoporosity”, Park, J.; Li, J.-R.; Sañudo, E.C.; Yuan, D.; Zhou, H.-C., *Chem. Commun.*, **2012**, *48* (6), 883 – 885.

7. “Stepwise Adsorption in a Mesoporous Metal-Organic Framework: Experimental and Computational Analysis” Yuan, D.; Getman, R.B.; Wei, Z.; Snurr, R.Q.; Zhou H.-C. *Chem. Comm.*, **2012**, *48*, 3297-3299.
8. “A Highly Porous and Robust (3,3,4)-Connected Metal-Organic Framework Assembled with a 90°-Bridging-Angle-Embedded Octa-carboxylate Ligand”, Lu, W.; Yuan, D.; Makal, T. A.; Li, J.-R.; Zhou, H.-C., *Angew. Chem. Int. Ed.*, **2012**, *124* (7), 1612-1616.
9. “Highly Potent Bactericidal Activity of Porous Metal-Organic Frameworks”, Zhuang, W.; Yuan, D.; Li, J.-R.; Luo, Z.; Zhou, H.-C.; Bashir, S.; Liu, J., *Adv. Healthcare Mater.*, **2012**, *1*, 225–238.

Presentations

1. “MOFs, MOPs, and PPNs: Porous Materials through Rational Design”, University of California at Berkeley, Oct. 18, 2011, Berkeley, California.
2. “MOFs, MOPs, and PPNs: Preparation and Application”, University of North Carolina, Chapel Hill, Nov. 8, 2011, Chapel Hill, North Carolina.
3. Featured Speaker, “MOFs, MOPs, and PPNs: Porous Materials through Rational Design”, ACS Southwest Regional Meeting, Nov. 10, 2011, Austin, Texas.
4. “Optically Controlled Hydrogen Adsorption in MOFs and MOPs”, Jinhee Park and Hong-Cai Zhou, 2011 Southwest Regional ACS meeting, Nov. 12, 2011, Austin, Texas.
5. “Metal-organic frameworks constructed from infinite zinc chains”, Yangyang Liu, and Hong-Cai Zhou, 2011 Southwest Regional ACS meeting, Nov. 12, 2011, Austin, Texas.
6. “New interweaving MOF possessing the Pt₃O₄-net topology based on a metalloligand”, Zhangwen Wei and Hong-Cai Zhou, 2011 Southwest Regional ACS meeting, Nov. 12, 2011, Austin, Texas.
7. “MOFs, MOPs, and PPNs: Preparation and Application”, Sichuan University, Nov. 17, 2011, Nov. 17, 2011, Chengdu, Sichuan, China.
8. “MOFs, MOPs, and PPNs: Preparation and Application”, Sichuan Normal University, Nov. 17, 2011, Nov. 17, 2011, Chengdu, Sichuan, China.
9. “MOFs, MOPs, and PPNs: Preparation and Application”, National University of Singapore, Nov. 22, 2011, 2011, Singapore.
10. “MOFs, MOPs, and PPNs: Preparation and Application”, Nanyang Technological University, Nov. 23, 2011, 2011, Singapore.
11. “MOFs, MOPs, and PPNs: Preparation and Application”, Agency for Science Technology & Research (A*Star), Nov. 24, 2011, 2011, Singapore.
12. “Building Metal-Organic Frameworks, One Cavity at a Time”, Invited Speaker – University of South Florida, Mar 8, 2012, Tampa, FL.