IV.C.1 A Biomimetic Approach to Metal-Organic Frameworks with High H_2 Uptake

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Fiscal Year (FY) 2011 Objectives

- Design, synthesize, and characterize metal-organic frameworks (MOFs) with active metal centers aligned in porous channels and accessible by H_2 molecules.
- Through optimized, cooperative binding, the MOFs are expected to have enhanced affinity to H_2.
- These MOFs can help to reach the DOE 2010 and ultimately 2015 hydrogen storage goal.

Technical Barriers

This project addresses the following technical barriers from the Storage section (3.3.4) 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 2015 system goals, primarily the gravimetric and volumetric storage goals, at or near ambient temperatures and moderate pressure for on-board vehicular hydrogen storage (Table 1).

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

Storage Parameter	Units	2010	2015	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 2011 Accomplishments

- A highly porous and robust 3,3,4-connected MOF (PCN-80) has been synthesized with a unique octa-topic ligand featuring 90°-angle-dicarboxylate moiety. PCN-80 has Brunauer-Emmett-Teller (BET) and Langmuir surface areas of 3,850 $m^2\ g^{-1}$ and 4,150 $m^2\ g^{-1}$, respectively. It exhibits high gas-uptake capacity for H_2 of 4.8 wt% (29 g L^{-1}) at 44 bar and 77 K.
- Porous polymer networks (PPNs) grafted with sulfonic acid (PPN-6-SO_3H) and its lithium salt (PPN-6-SO_3Li) exhibit dramatic increase in isosteric heats of hydrogen-adsorption.
- Highly stable PPNs are synthesized through Yamamoto homo-coupling reaction between tetrahedral monomers. Among those polymers, PPN-4 shows exceptionally high Langmuir surface area of 10,063 $m^2\ g^{-1}$ (SA_{BET}: 6,461 $m^2\ g^{-1}$). It also exhibits ultra-high hydrogen storage capacity (8.3 wt% at 55 bar and 77 K).

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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 adsorption. 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_2 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 H_2-hosting void in a three-dimensional framework so that they can interact directly with the guests (H_2 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 H_2 storage capacity in MOFs. (9) Incorporated polyyne unit into MOFs, which has higher H_2 affinity. (10) Design and synthesize PPNs with high chemical stability suitable for further decoration. (11) 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 applications in hydrogen storage. Table 2 shows the comparison of hydrogen uptakes of selected MOFs and PPNs. Next we will discuss in detail the results of H_2 uptakes of these materials.

Functional MOFs Based on MOF-177

As we all know, MOF-177 is a porous material with high surface area ($SA_{Langmuir}$: 5,640 $m^2\ g^{-1}$) and high hydrogen storage (7.0 wt% at 60 bar and 77 K). Our tactics for preparing the functionalized MOF is to construct isostructural MOF-177 by designing a new functional organic ligand with the methyl, amino, hydroxyl and chiral group (Figure 1a). As expected, the four new ligands reacted with zinc salt to form four novel MOFs with isostructural MOF-177 (Figure 1b). Based on the N_2 sorption isotherm, PCN-103(N) has a BET surface area of 4,300 $m^2\ g^{-1}$ ($SA_{Langmuir}$: 5,500 $m^2\ g^{-1}$) and a total pore volume of 1.95 $cm^3\ g^{-1}$, which is similar to those results of MOF-177. PCN-103(O) has a BET surface area of 2,866 $m^2\ g^{-1}$ ($SA_{Langmuir}$: 4,587 $m^2\ g^{-1}$), while PCN-103(Ch) a BET surface area of 2,850 $m^2\ g^{-1}$ ($SA_{Langmuir}$: 4,144 $m^2\ g^{-1}$) (Figure 1c). The saturated excess gravimetric H_2 uptake of PCN-103(N) is 5.60 wt% at 40 bar, PCN-103(Ch) has a saturated excess gravimetric H_2 uptake of 5.10 wt% at 50 bar, while PCN-103(O) has a saturated excess gravimetric H_2 uptake of 5.40 wt% at 45 bar (Figure 1d).

TABLE 2. Comparison of Hydrogen Uptakes of Selected MOFs and PPNs

Material	ΔH_{ads} (kJ/mol)	H_2 Adsorption			
		Gravimetric H_2 Uptake (wt%)	Volumetric H_2 Uptake (g/L)	T (K)	P (bar)
PCN-26	6.81	2.86	24.7	77	32
PCN-69	8.14	5.20	19.5	77	50
PCN-103(N)	6.60	5.60	25.6	77	40
PCN-103(O)	-	5.40	24.6	77	45
PCN-103(Ch)	-	5.10	26.0	77	50
PCN-80	5.20	4.80	29.0	77	44
PCN-46	7.20	5.31	32.3	77	32
PPN-4	4.0	8.34	28.2	77	55

A Robust MOF with Flexible Octatopic Ligand

A newly designed flexible octatopic carboxylic acid ligand, tetrakis[(3,5-dicarboxyphenyl)-oxamethyl]methane acid (H_8TDM) has been used to react with $CuBr_2$ affording an MOF, $Cu_4(H_2O)_4(TDM)\cdot xS$ (PCN-26, S presents non-coordinated solvent molecules). PCN-26 was constructed by two different types of cages, octahedral and cuboctahedral, to form a polyhedron-stacked three-dimensional framework with open channels in three directions. In PCN-26, both $[Cu_2(O_2CR)_4]$ secondary building units (SBUs) and quaternary carbon atoms of TDM^{8-} act as four-connected nodes, while the CH_2O-isophthalate moieties act as three-connected nodes, the framework is a 3-nodal net and adopts a new network topology with the Schläfli symbol of $\{3^{11}.4^{10}.5^7\}_4\{3^2.6^2.7^2\}_2\{3^6\}$. Three-dimensional square channels are observed from the *a*, *b* and *c* axis with the sizes of 7.57 × 7.57 Å, 8.13 × 8.13 Å and 7.93 × 7.93 Å, respectively. N_2 sorption measurements were performed at 77 K, 1 bar, giving a Langmuir surface area of 2,545 $m^2\ g^{-1}$, a BET surface area of 1,854 $m^2\ g^{-1}$, and total pore volume of 0.84 $cm^3\ g^{-1}$.

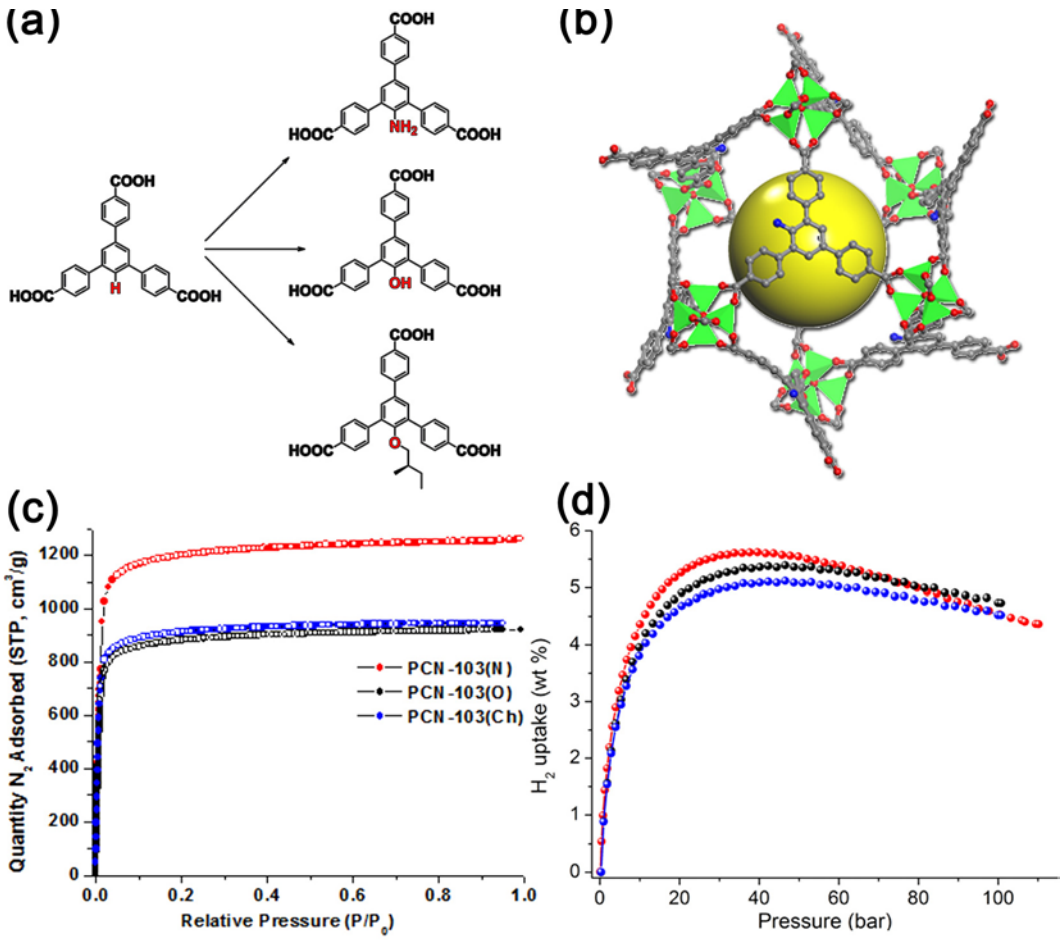

FIGURE 1. (a) The design of functional ligands; (b) the structure of PCN-103; (c) the N_2 isotherms of PCN-103(X) at 77 K; (d) the H_2 uptakes for PCN-103(X) at 77 K and high pressure range.

The PCN-26 has a saturated excess gravimetric hydrogen adsorption of 2.86 wt% at 77 K and 32 bar, with a hydrogen-adsorption enthalpy of 6.81 kJ mol^{-1}.

A Highly Porous and Robust 3,3,4-Connected MOF Assembled with a 90°-Angle-Embedded Octa-carboxylate Ligand

The octa-carboxylate ligand, BTTCD, 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 3,3',5,5'-tetrabromo-1,1'-biphenyl followed by hydrolysis with potassium hydroxide in an overall yield of 30%. Solvothermal reaction of H_8BTTCD and $Cu(NO_3)_2$•2.5H_2O in N,N-dimethylformamide (DMF) in the presence of HBF_4 afforded tetragonal-shaped green crystals of PCN-80 with molecular formula $[Cu_2(BTTCD)]$•2DMF. PCN-80 crystallizes in tetragonal I4/mmm space group with a = b = 23.057(2), c = 30.762(3) Å. In the structure of PCN-80, the novel BTTCD ligand contains four 90°-angle subunits (Figure 2a) where the carbazole ring is perpendicular to the central benzene ring and the dihedral angle between adjacent carbazole rings is 47.4°. Every BTTCD ligand utilizes eight carboxylate groups to link eight 4-connected dicopper paddlewheel SBUs (Figure 2b) in a rectangular prismatic fashion to generate a porous (3,3,4)-connected network. There are three kinds of microporous cages with different sizes. L-cages (16.6 Å in diameter) are formed by eight $[Cu_2(O_2CR)_4]$ SBUs, and twelve BTTCD linkers (Figure 2c); M-cages (13.4 Å) from eight SBUs and four BTTCD linkers (Figure 2d); and S-cages (7.6 Å) through four SBUs and two BTTCD ligands (Figure 2e). The overall structure consists of these three types of cages packed in a 1:1:1 ratio (Figure 2f). From the viewpoints of topology, the SBUs serve as 4-connected nodes, whereas BTTCD ligands as 3,3-connected nodes. As a result, PCN-80 adopts the very rare 3,3,4-c 3-nodal net (Figure 2g) with topological point symbol of $\{7^2.8^2.11^2\}\{7^2.8\}\{7^3\}_2$, which is previously unreported.

The calculated free volume in fully desolvated PCN-80 is 72.1% by *PLATON* (1.8 Å probe radius), and pore volume is 1.25 cm^3 g^{-1}. To confirm the porosity of PCN-80, a fully desolvated sample was degassed under dynamic vacuum

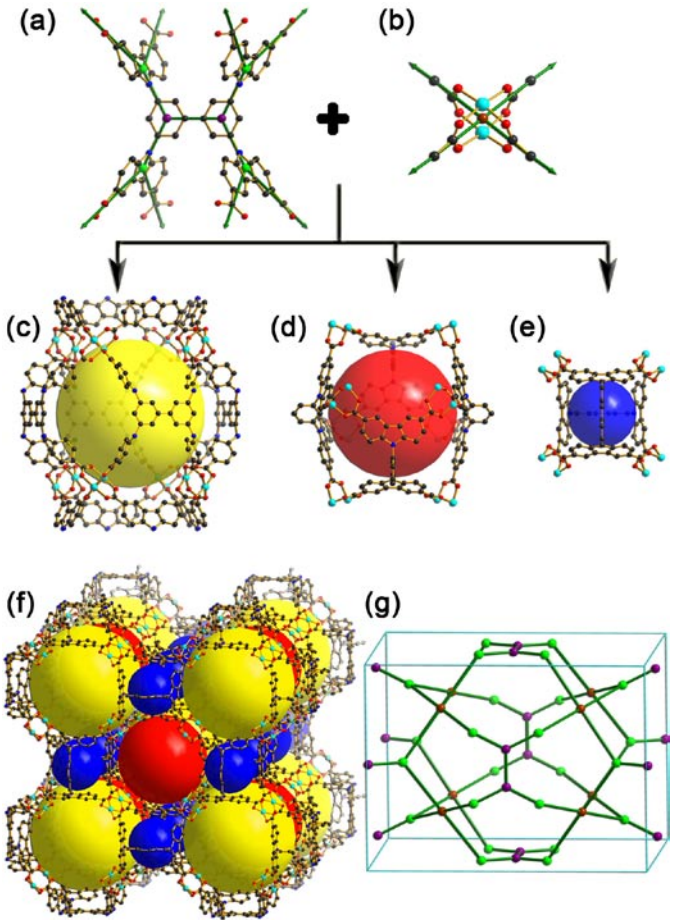

FIGURE 2. (a) 8-connected BTTCD ligand; (b) 4-connected dicopper paddlewheel SBU; (c) large size cage (L-cage); (d) middle size cage (M-cage); (e) small size cage (S-cage); (f) cages and their three-dimensional packing in PCN-80; (g) topology of PCN-80.

at 80°C for 10 h after solvent exchange with methanol and then dichloromethane. A color change from green to deep-purple-blue was observed, typical for dicopper-paddlewheel frameworks in which open copper sites are generated. The N_2 sorption for PCN-80 at 77 K exhibited a reversible *Type-I* isotherm, a characteristic of microporous materials. The estimated apparent BET surface area was ~3,850 $m^2 g^{-1}$ (calculated ~3,584 $m^2 g^{-1}$) and Langmuir surface area ~4,150 $m^2 g^{-1}$, which is similar to PCN-66 (BET ~4,000 $m^2 g^{-1}$), among the highest reported to date for porous MOFs or covalent organic frameworks. Notably, the experimental surface area of PCN-80 perfectly agrees with that calculated using Material Studio 5.5. On the basis of the N_2 sorption isotherm, PCN-80 has a calculated total pore volume of 1.47 $cm^3 g^{-1}$. Calculated with N_2 isotherm using DFT methods, the pore size distribution for PCN-80 indicates three different kinds of pores with diameters of 7.3, 11.8, and 14.5 Å, respectively, which is in good agreement with the crystal data.

In the low-pressure region, it is well known that the H_2-uptake capacity is mainly controlled by the hydrogen affinity towards the framework. PCN-80 exhibits H_2-uptake capacity as high as 2.3 wt% at 77 K and 1 bar, which is among the highest at low pressure. The excellent performance of PCN-80 can be largely attributed to its microporous nature as well as high open-metal-site density upon activation. High-pressure gas sorption was performed on PCN-80 using volumetric measurement method. At 77 K, the excess H_2-uptake capacity of PCN-80 reached its maximum value of 4.8 wt% (29 g L^{-1}) at 44 bar. Based on a variant of the Clausium-Clapeyron equation, the H_2 isosteric adsorption enthalpy of PCN-80 reaches 5.2 kJ mol^{-1} at low coverage.

Highly Stable Porous Polymer Networks with Exceptionally High H_2-Uptake Capacities

Conventional Yamamoto homo-coupling reaction for polymerization was carried out at 80°C with DMF as the solvent. However, when the same reaction condition was applied to tetrakis(4-bromophenyl)silane or tetrakis(4-bromophenyl)admantane, the surface areas of the synthesized materials were much lower than the calculated data. With the assumption that reduced temperature would slow down the reaction to yield polymers with higher molecular weight and avoid any unwanted side reactions, we adopted an optimized Yamamoto homo-coupling procedure, in which the reactions were carried out at room temperature in a DMF/tetrahydrofuran mixed solvent. Using this procedure, we were able to synthesize PPN-3 (X: admantane), PPN-4 (X: silicon), and PPN-5 (X: germanium) with exceptionally high surface areas (Figure 3a and 3b). The surface area of PPN-3 synthesized through this procedure is much higher than the value previously reported, and the surface area of PPN-4 is close to the value predicted based on the molecular model, indicating the excellence of this optimized procedure. With the BET surface area of 6,461 $m^2 g^{-1}$ and Langmuir surface area of 10,063 $m^2 g^{-1}$, PPN-4 possesses, to the best of our knowledge, the highest surface area among all the reported porous materials so far. In addition, most of the pores in PPN-4 sit with the range of microporous or microporous/mesoporous range, which serves remarkably for gas storage purposes.

As the previously reported PPNs, PPN-3, PPN-4, and PPN-5 are off-white powders, not soluble in common organic solvents. There is no residual bromine from the elemental analysis result, indicating the completion of the reaction and the efficiency of Yamamoto homo-coupling. Surprisingly, a trace amount of nitrogen was detected in PPN-3 and PPN-5 (0.14 wt% and 0.11 wt%, respectively), which probably comes from the trapped 2,2'-bipyridine within the shrunken pores caused by network interpenetration. This network interpenetration may also account for the reduced experimental surface areas of PPN-3 and PPN-5 compared with the calculated data. Thermogravimetric analysis data show the three polymers possess good thermal stability and high decomposition temperatures of more than 450°C in a nitrogen atmosphere.

In addition, PPN-4 retains its structural integrity after being exposed to air for one month, as indicated by virtually no drop of N_2 uptake capacity at 77 K.

The exceptionally high surface area combined with excellent stability make PPN-4 a very attractive candidate for gas storage applications, particularly in H_2 for clean energy purposes. To evaluate its gas storage capacity, high-pressure excess adsorption of H_2 within PPN-4 were measured at 77 K (liquid nitrogen bath). As shown in Figure 3c, the excess H_2 uptake of PPN-4 at 77 K and 55 bar can reach 91 mg g^{-1} (8.34 wt%, total uptake: 158 mg g^{-1}, 13.6 wt%, 80 bar), which is by far the highest among all amorphous materials, and is also comparable to the best value reported in MOFs. The isosteric heat of adsorption for H_2 is around 4 kJ mol^{-1} (Figure 3d), which fits within the range of physisorption and indicates that the high surface area might be the sole factor in determining this high H_2 uptake capacity. Unlike MOFs, whose H_2 uptake capacity will decrease after several uptake-release cycles, the H_2 uptake capacity of PPN-4, even being exposed to air for several days, can be simply regenerated by heating under vacuum. The excellent physicochemical stability and impressively high delivery capacity (71 mg g^{-1}, 77 K, from 1.5 bar to 55 bar) make PPN-4 the currently unbeatable material for cryogenic H_2 storage application.

Post-Grafting Porous Polymer Networks for Hydrogen Storage

Theoretical studies on MOF and PPN materials have suggested that introduction of light, non-transition metal ions such as Li^+, Na^+ or Mg^{2+} might afford non-dissociative hydrogen binding, thus enhancing overall adsorption of H_2. In particular, Li-doped materials appear to be especially interesting in this regard. Here we report the post-grafting of PPN-6 with sulfonic acid and lithium sulfonate. PPN-6 (also known as porous aromatic framework [PAF]-1) was synthesized using an optimized Yamamoto homo-coupling reaction of tetrakis(4-bromophenyl)methane. The default diamondoid framework topology imposed by the tetrahedral monomers provides widely open and interconnected pores to efficiently prevent the formation of "dead space", more importantly, the extremely robust all-carbon scaffold of the network can stand harsh reaction conditions and makes it perfect to build up polar organic groups on the biphenyl units; indeed, by reacting with chlorosulfonic acid in dichloromethane, PPN-6 was modified into PPN-6-SO_3H,

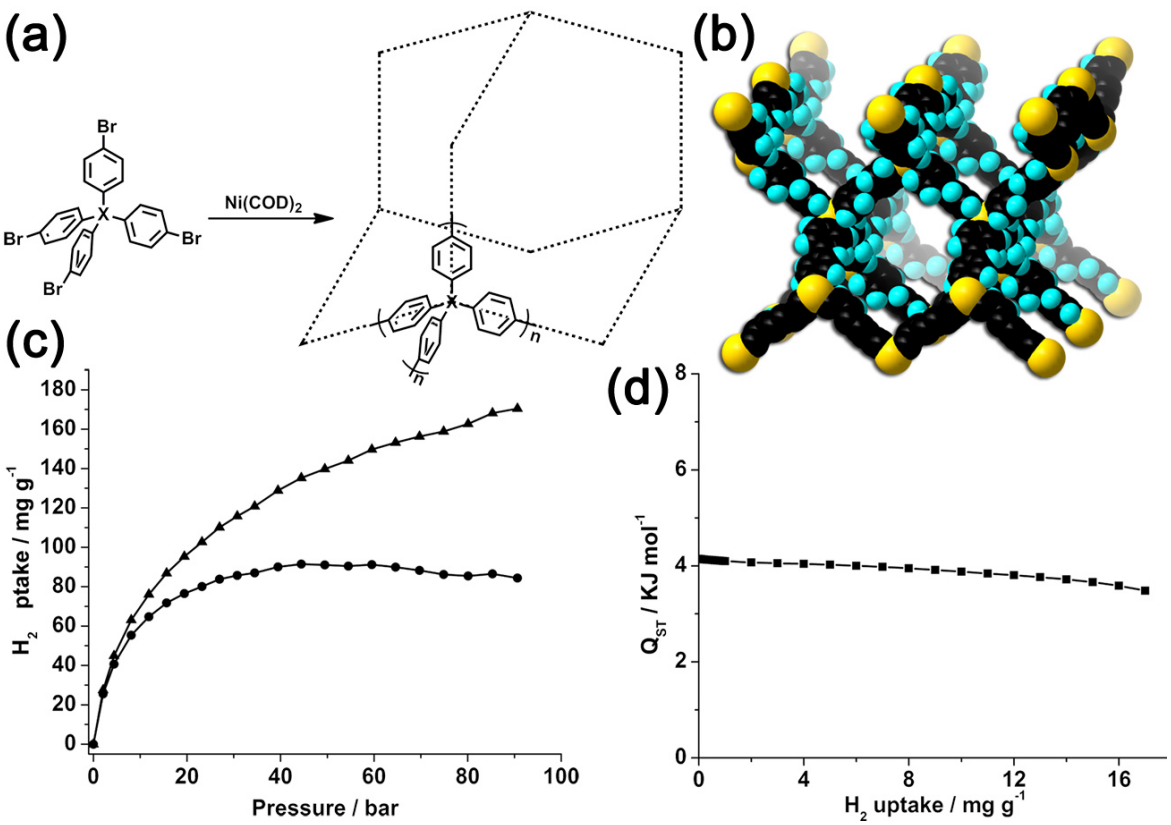

FIGURE 3. (a) Synthetic route for PPN-3 (X: Adamantane), PPN-4 (X: Si), PPN-5 (X: Ge), and PAF-1 (X: C); (b) The default noninterpenetrated diamondoid network of PPN-4 (black, C; cyan, H; yellow, Si); (c) Excess and total H_2 adsorption isotherms of PPN-4 at 77 K; (d) Isosteric heat of adsorption for H_2 in PPN-4.

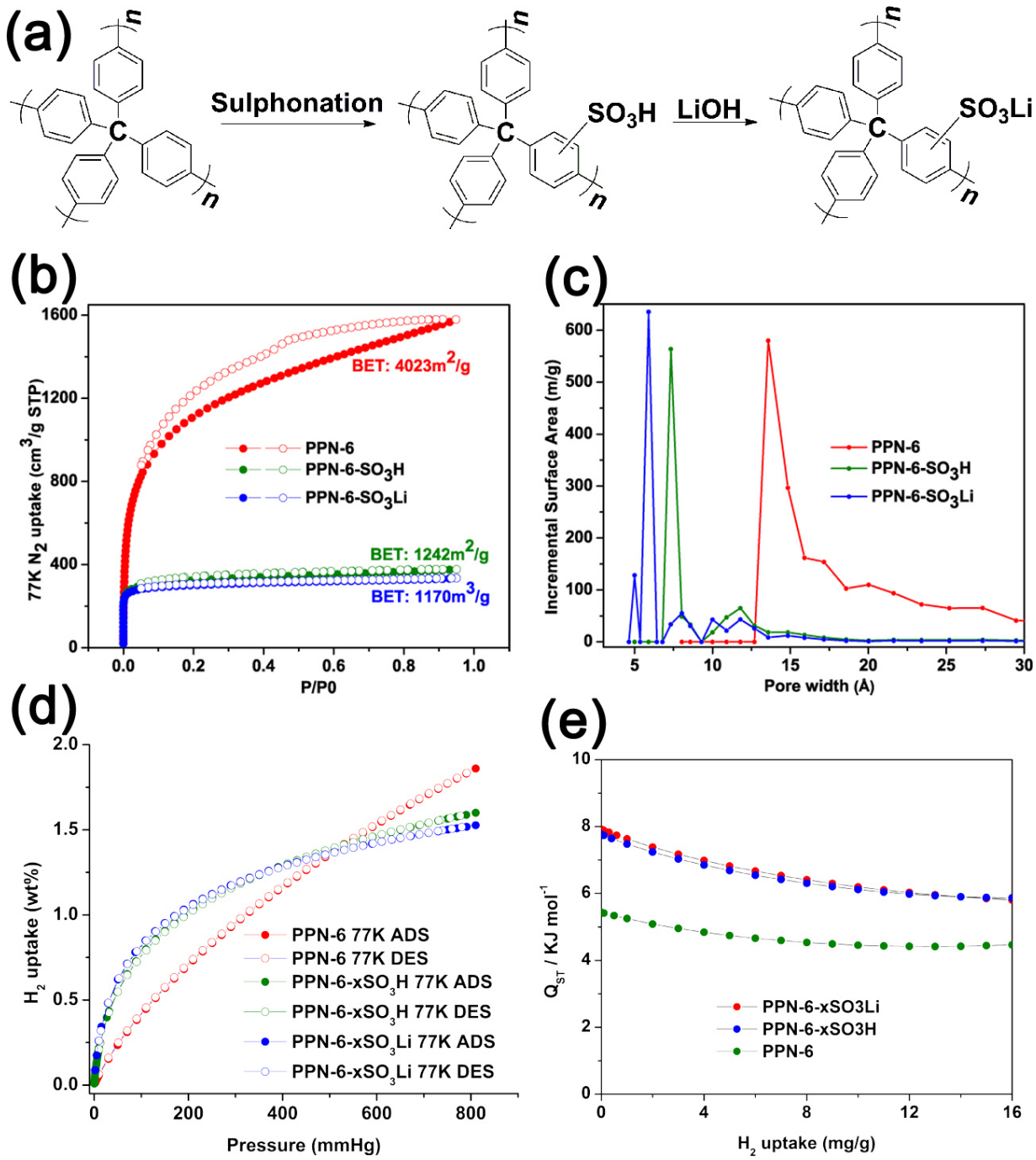

FIGURE 4. (a) Synthesis and post-synthetic grafting of PPN-6-X; (b) (a) N_2 adsorption (closed)/desorption (open) isotherms of PPN-6-X at 77 K; (c) Pore size distribution curves of PPN-6-X; (d) Excess adsorption isotherms of PPN-6-X at 77 K; (d) Isosteric heat of adsorption for H_2 in PPN-6-X.

which was further neutralized to produce PPN-6-SO_3Li (Figure 4a). Nitrogen gas adsorption/desorption isotherms of the three networks were collected at 77 K (Figure 4b). Notably, the huge hysteresis in PPN-6 adsorption/desorption isotherm disappeared into nearly type-I isotherms in functionalized PPN-6. The BET surface areas were calculated from the adsorption branch of the nitrogen isotherms over a BET-theory-satisfied pressure range and were found to be 4,023, 1,242, and 1,170 $m^2\ g^{-1}$ for PPN-6, PPN-6-SO_3H and PPN-6-SO_3Li, respectively. The pore size distributions of the three networks have been calculated with their N_2 adsorption isotherms at 77 K (Figure 4c). Along with the decrease of surface area, the pore size becomes progressively reduced with aromatic sulfonation and lithiation. Recent studies have indicated several features that are desirable for enhancing storage capacity of small gas molecules. One such feature is the suitable pore size commensurate with the size of gas molecule. The relatively

small pore sizes of functionalized PPN-6 fall into the range of 5.0-10.0 Å. Though the experimental BET surface of PCN-6-SO_3Li area decreased, the H_2 isosteric heat increased 47% (Figure 4d and 4e), which is consistent with theoretical calculation. The introduction of other metal will also be studied, such as Mg, Ti, Ni, Co and so on.

Conclusions and Future Directions

Conclusions:

- Constructing new MOFs using 90°-angle-embedded octa-carboxylate ligand is proved as a general approach towards stable MOFs with high surface areas and high hydrogen uptake.
- PPNs with tunable pore size and surface area can be prepared with high chemical and thermal stability, which are good candidate for hydrogen storage.
- PPN postsynthetic modification and metal incorporation can remarkably enhance the heat of adsorption.

Future Directions:

- Further enhancement of H_2-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 will be tested.
- Working with partners, test H_2 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.

Special Recognitions & Awards

1. DOE Hydrogen Program Special Recognition Award as a member of the Hydrogen Sorption Center of Excellence (HSCoE), 2010.

FY 2011 Publications/Presentations

1. "The current status of hydrogen storage in metal–organic frameworks–updated", Sculley, J.; Yuan, D.; Zhou, H.-C., *Energy Environ. Sci.*, **2011**, *4*, 2721-2735.

2. "Construction of Two 3D Homochiral Frameworks with 1D Chiral Pores via Chiral Recognition", Li, H.-Y.; Jiang, L., Xiang, H.; Makal, T.; Zhou, H.-C.; Lu, T.-B., *Inorg. Chem.*, **2011**, *50*, 3177-3179.

3. ''Surface functionalization of metal-organic polyhedron for homogeneous cyclopropanation catalysis", Lu, W.; Yuan, D.; Yakovenko, A.; Zhou, H.-C., *Chem. Comm.*, **2011**, 47, 4968-4970.

4. "Metal-Organic Frameworks", Makal, T.A.; Yuan, D.; Zhao, D.; Zhou, H.-C., In *The Chemistry of Nanostructured Materials*, Vol. II Yang, P.; Ed. World Scientific: Singapore, **2011**, 37-64.

5. "Carbon Dioxide Capture-Related Gas Adsorption and Separation in Metal-Organic Frameworks", Li, J.-R.; Ma, Y.; McCarthy, M.C.; Sculley, J.; Yu, J.; Jeong, H.-K.; Balbuena, P.B.; Zhou, H.-C., *Coord. Chem. Rev.*, **2011**, *255*, 1791-1823.

6. "Tune the Topology and Functionality of Metal-Organic Frameworks by Ligand Design", Zhao, D.; Timmons, D.J.; Yuan, D.Q.; Zhou, H.-C., *Accounts Chem. Res.*, **2011**, *44*, 123-133.

7. "Surface Functionalization of Porous Coordination Nanocages Via Click Chemistry and Their Application in Drug Delivery", Zhao, D.; Tan, S.W.; Yuan, D.Q.; Lu, W.G.; Rezenom, Y.H.; Jiang, H.L.; Wang, L.Q.; Zhou, H.-C., *Adv. Mater.*, **2011**, *23*, 90-93.

8. "A Stepwise Transition From Microporosity to Mesoporosity in Metal-Organic Frameworks by Thermal Treatment", Yuan, D.; Zhao, D.; Timmons, D.J.; Zhou, H.-C., *Chem. Sci.*, **2011**, *2*, 103-106.

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10. "Ligand Bridging-Angle-Driven Assembly of Molecular Architectures Based on Quadruply Bonded Mo–Mo Dimers", Li, J.-R.; Yakovenko, A.; Lu, W.; Timmons, D.J.; Zhuang, W.; Yuan, D.; Zhou, H.-C., *J. Am. Chem. Soc.*, **2010**, *132*, 17599-17610.

11. "Recent Advances in the Study of Mesoporous Metal-Organic Frameworks", Fang, Q.-R.; Makal, T. A.; Young, M.D.; Zhou, H.-C., *Comments on Inorganic Chemistry*, **2010**, *31*, 165-195.

12. "Porous Polymer Networks: Synthesis, Porosity, and Applications in Gas Storage/Separation", Lu, W.; Yuan, D.; Zhao, D.; Schilling, C.I.; Plietzsch, O.; Muller, T.; Brase, S.; Guenther, J.; Blumel, J.; Krishna, R.; Li, Z.; Zhou, H.-C., *Chem. Mater.*, **2010**, *22*, 5964-5972.

13. "Bridging-Ligand-Substitution Strategy for the Preparation of Metal–Organic Polyhedra", Li, J.-R.; Zhou, H.-C., *Nature Chem.*, **2010**, *2*, 893-898.

14. "Two Robust Porous Metal–Organic Frameworks Sustained by Distinct Catenation: Selective Gas Sorption and Single-Crystal-to-Single-Crystal Guest Exchange", Yang, R.; Li, L.; Xiong, Y.; Li, J.-R.; Zhou, H.-C.; Su, C.-Y., *Chem.-Asian J.*, **2010**, *5*, 2358-2368.

15. "Thermosensitive Gating Effect and Selective Gas Adsorption in a Porous Coordination Nanocage", Zhao, D.; Yuan, D.; Krishna, R.; Van Baten, J.M.; Zhou, H.-C., *Chem. Commun.*, **2010**, *46*, 7352-7354.

16. "Control over Interpenetration in Lanthanide–Organic Frameworks: Synthetic Strategy and Gas-Adsorption Properties", He, H.Y.; Yuan, D.Q.; Ma, H.Q.; Sun, D.F.; Zhang, G.Q.; Zhou, H.-C., *Inorg. Chem.*, **2010**, *49*, 7605-7607.