

## Metal–Organic Frameworks with Functional Pores for Recognition of Small Molecules

BANGLIN CHEN,<sup>\*,†</sup> SHENGCHANG XIANG,<sup>†</sup> AND  
GUODONG QIAN<sup>\*,‡</sup>

<sup>†</sup>Department of Chemistry, University of Texas at San Antonio, San Antonio, Texas 78249-0698, <sup>‡</sup>State Key Laboratory of Silicon Materials, Department of Materials Science & Engineering, Zhejiang University, Hangzhou 310027, China

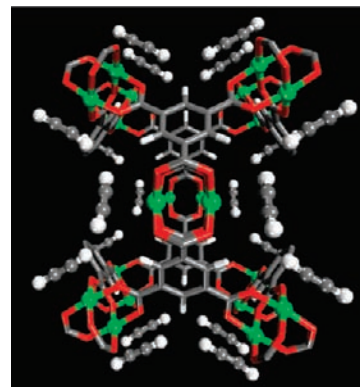
RECEIVED ON JANUARY 27, 2010

### CON SPECTUS

**M**olecular recognition, an important process in biological and chemical systems, governs the diverse functions of a variety of enzymes and unique properties of some synthetic receptors. Because molecular recognition is based on weak interactions between receptors and substrates, the design and assembly of synthetic receptors to mimic biological systems and the development of novel materials to discriminate different substrates for selective recognition of specific molecules has proved challenging. The extensive research on synthetic receptors for molecular recognition, particularly on noncovalent complexes self-assembled by hydrogen bonding and metal–organic coordination, has revealed some underlying principles. In particular, these studies have demonstrated that the shapes of the supramolecular receptors play significant roles in their specific and selective recognition of substrates: receptors can offer concave surfaces that complement their convex targets.

This Account describes our research to develop a synthetic molecular recognition platform using porous metal–organic frameworks (MOFs). These materials contain functional pores to direct their specific and unique recognition of small molecules through several types of interactions: van der Waals interactions of the framework surface with the substrate, metal–substrate interactions, and hydrogen bonding of the framework surface with the substrate. These materials have potential applications for gas storage, separation, and sensing. We demonstrate a simple strategy to construct a primitive cubic net of interpenetrated microporous MOFs from the self-assembly of the paddlewheel clusters  $M_2(\text{CO}_2)_4$  ( $M = \text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Co}^{2+}$ ) with two types of organic dicarboxylic acid and pillar bidentate linkers. This efficient method allows us to rationally tune the micropores to size-exclusively sort different small gas molecules, leading to the highly selective separation and purification of gases. By optimizing the strong interactions between open metal sites within porous MOFs and gas molecules such as hydrogen and acetylene, we have developed several MOF materials with extraordinary acetylene storage capacity at room temperature. We have also immobilized Lewis acidic and basic sites into luminescent porous MOFs to recognize and sense neutral and ionic species. Using the strategy to systematically immobilize different open metal sites within porous MOFs from the metalloligand precursors, we have developed the first microporous mixed-metal–organic framework (M'MOF) with enhanced affinity for hydrogen molecules, which successfully separated  $\text{D}_2$  from  $\text{H}_2$  using kinetic isotope quantum molecular sieving.

Because we can functionalize the pores to direct their specific recognition of small molecules, the emerging porous MOFs serve as novel functional materials for gas storage, separation, heterogeneous catalysis, and sensing.



### 1. Introduction

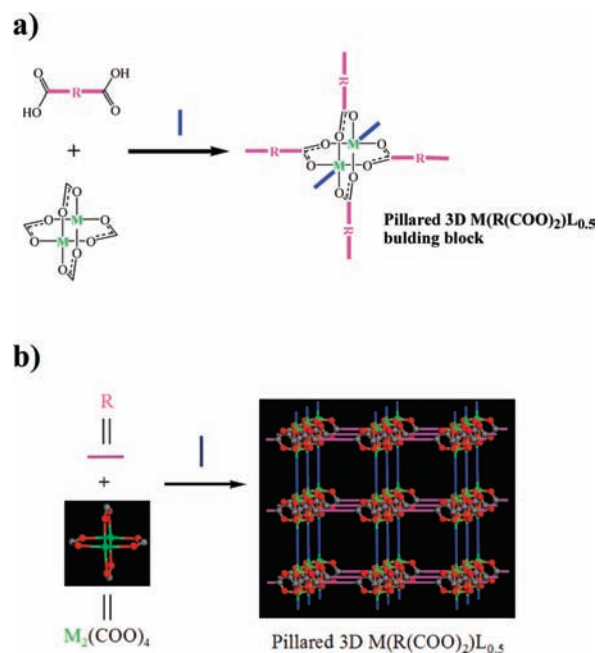
The emergence of a new type of porous metal–organic framework (MOF) materials has significantly enriched the porous material domains, and research on porous MOFs been one

of the most active endeavors among the inorganic and materials chemistry community over the past two decades, as clearly shown in the increasing numbers of scientific publications.<sup>1–56</sup> Such porous MOFs can be self-assembled straightfor-

wardly by the metal ions/metal clusters with organic linkers by the coordination bonds. Unlike the classical porous zeolite aluminum silicates whose components are restricted to  $\text{Al}^{3+}/\text{Si}^{4+}$  and  $\text{O}^{2-}/\text{OH}^-$  to construct porous structures, the rich inorganic and organic building blocks to construct porous MOFs have provided the bright promise to synthesize an infinite number of new porous materials of diverse structures and porosity. In fact, a large number of porous MOFs have been realized with the pores ranging from 2 to 47 Å. The moderate coordination bond energies, variable metal coordination geometries, and flexible organic linkers have further provided the unique flexible nature of some porous MOFs whose structures and properties can be tuned by external stimuli such as temperature and pressure.<sup>13,14</sup>

The potential to construct porous structures of coordination polymers by the coordination bonds was initially proposed in 1989;<sup>1</sup> however, it took almost 10 years to realize the first few porous MOFs with permanent porosity established by gas adsorption studies,<sup>2–4</sup> as exemplified by MOF-5 in 1999 with significantly high surface area of greater than 3000  $\text{m}^2/\text{g}$ . The implementation of simple solvothermal synthesis and incorporation of large organic linkers to assemble highly porous MOF-14 in 2001, to some extent, has highlighted the establishment of a general strategy to construct porous MOFs.<sup>5,6</sup> Since then, the research endeavors have been mainly focused on the realization of functional pores and thus their specific properties and applications on gas storage, separation, heterogeneous catalysis, sensing, etc.<sup>7–56</sup> The term “coordination polymer” focuses on the bonding nature between the metal ions and bridging organic linkers and structurally polymeric features. The term “metal–organic framework” highlights the similarity with the traditional framework solids, particularly zeolite framework materials, and thus emphasizes the robustness and the porosity. There is some overlap between these two terms. Generally, “coordination polymer” is broader, while “metal–organic framework” is more specific.

Specific and unique molecular recognition between host porous MOFs and guest substrates is the design criteria to construct porous MOFs with functional pores to direct their functional properties and applications. Generally speaking, the pores within MOFs can be functionalized by tuning the pore/window sizes to make use of size-exclusive effects for the separation and purification of small molecules and can be optimized or maximized to fully make use of the pore space for the storage of gas molecules. To immobilize functional sites such as Lewis basic or acidic and open metal sites within porous MOFs to introduce their specific recognition of small

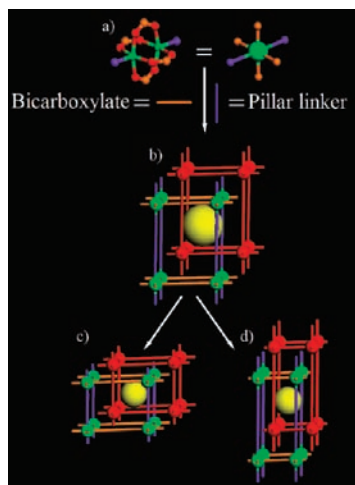


**FIGURE 1.** (a) Building block and (b) assembled 3D  $\text{M}(\text{R}(\text{COO})_2)\text{L}_{0.5}$  framework of the proposed microporous hybrid materials with 3D primitive cubic-type structures.

substrates, it is expected that we will be able to target some unique porous MOFs with multifunctional properties and applications. This Account focuses on our research on porous MOFs with functional pores for recognition of small molecules and thus their applications in gas storage, separation, and sensing. Specifically, three approaches have been developed: (1) rationally tuned micropores within MOFs of a primitive cubic net for highly selective separation of gas molecules; (2) functional sites within porous MOFs for high gas storage and highly sensitive sensing of small substrates; (3) construction of porous mixed-metal–organic frameworks ( $\text{M}'\text{MOFs}$ ) to immobilize open metal sites for gas storage and separation.

## 2. Rationally Tuned Micropores within MOFs of a Primitive Cubic Net for Highly Selective Separation of Gas Molecules

Deliberate control and tuning of small pore/window sizes within porous MOFs is very crucial to induce highly efficient separation of gas molecules by the size-exclusion effect in which small substrates can go through the pore channels while large ones are blocked. In this regard, the simple strategy to construct primitive cubic nets from paddle-wheel clusters and two types of organic linker, dicarboxylic acid and pillar bidentate organic linker, is particularly of interest and importance.<sup>30,31</sup> As shown in Figure 1, incorporation of paddle-wheel clusters  $\text{M}_2(\text{CO}_2)_4$  with bicarboxylates leads to two-dimensional grid sheet  $\text{M}_2(\text{R}(\text{COO})_2)_2$  ( $\text{M} = \text{Cu}^{2+}, \text{Zn}^{2+}$ , and



**FIGURE 2.** Schematic illustration of (a) paddle-wheel  $M_2(\text{COO})_4$  cluster as an octahedral node to form (b) a doubly interpenetrated primitive cubic framework whose pore void spaces can be reduced and tuned by (c) shorter pillar organic linker L and (d) shorter bicarboxylate organic linker  $R(\text{COO})_2$ .

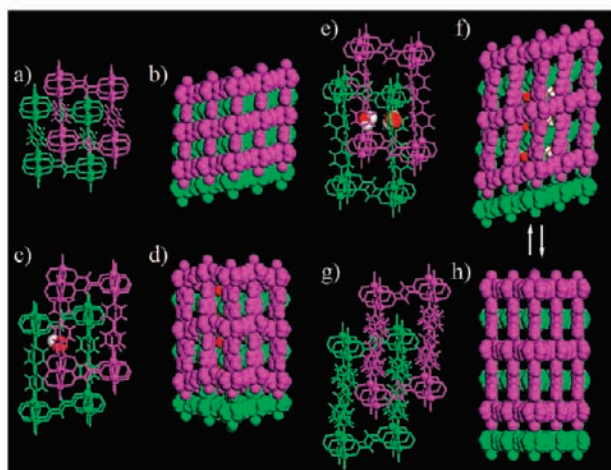
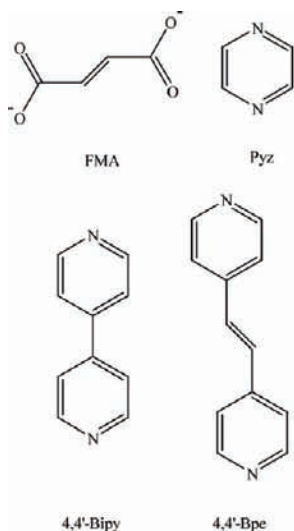
$\text{Co}^{2+}$ ; R = bridging unit). These sheets can be further pillared by the bridging linker L to form highly robust microporous pillared MOFs  $M(R(\text{COO})_2)_L$  with 3D primitive cubic-type structures (Figure 1).

The pores within such 3D primitive cubic type MOFs are predetermined by the different combinations of bicarboxylates and pillar linkers. The very unique feature of such an approach is that by making use of framework interpenetration, the small micropores can be easily realized and tuned for their highly selective separation and purification of small molecules. As shown in Figure 2, the small micropores in Figure

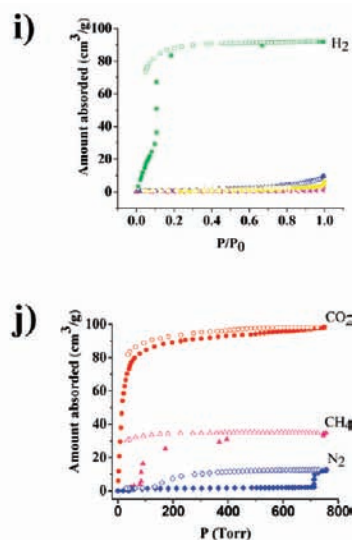
2b can be simply tuned and narrowed by either utilizing shorter pillar organic linker L (Figure 2c) or shorter bicarboxylate organic linker  $R(\text{COO})_2$  (Figure 2d). Over the past several years, we have realized a series of such 3D primitive cubic type MOFs of variable pore sizes from 2 to 7 Å.<sup>32–40</sup> Two representative examples for their highly selective separation of small molecules are shown below.

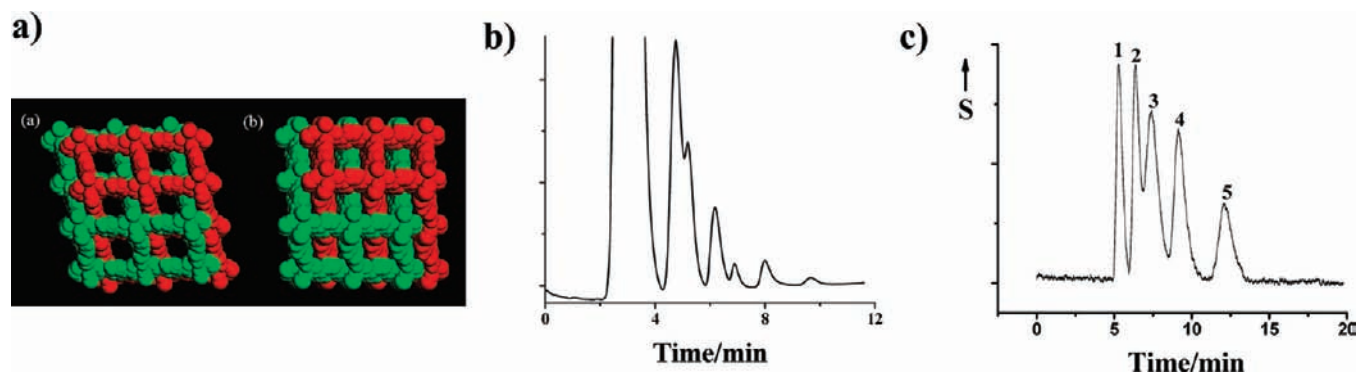
### 2.1. Rationally Designed Micropores for Selective Sorption of Gas Molecules.

Self-assembly of paddle-wheel clusters  $\text{Cu}_2(\text{CO}_2)_4$  with fumarate (FMA) leads to 2D square grid nets, which are further pillared by organic linker pyrazine (Pyz), 4,4'-bipyridine (4,4'-Bipy), and 4,4'-Bpe = *trans*-bis(4-pyridyl)-ethylene (4,4'-Bpe) to form 3D doubly interpenetrated primitive cubic frameworks  $\text{Cu}(\text{FMA})(\text{Pyz})_{0.5}$ ,  $\text{Cu}(\text{FMA})(4,4'\text{-Bipy})_{0.5} \cdot 0.25\text{H}_2\text{O}$  and  $\text{Cu}(\text{FMA})(4,4'\text{-Bpe})_{0.5} \cdot 0.5 \text{H}_2\text{O}$ , respectively. As expected above, the formed void spaces have been rationally and systematically tuned from condensed (Figure 3b), to pore aperture of  $1.4 \times 1.8 \text{ \AA}^2$  (Figure 3d) and  $2.0 \times 3.2 \text{ \AA}^2$  (Figure 3f), simply by increasing the pillar linker length, as revealed in their single X-ray crystal structures. Sorption studies further confirm that  $\text{Cu}(\text{FMA})(4,4'\text{-Bpe})_{0.5}$  shows selective sorption behavior with respect to different gas molecules (Figure 3i,j); the very few rationally designed microporous MOFs for selective gas sorption. The ultramicropores of  $2.0 \times 3.2 \text{ \AA}^2$  within  $\text{Cu}(\text{FMA})(4,4'\text{-Bpe})_{0.5}$ , which are larger than the size of  $\text{H}_2$  (2.8 Å) but smaller than those of CO (3.76 Å) and  $\text{N}_2$  (3.64 Å), differentiate the significantly higher  $\text{H}_2$  uptake from CO and  $\text{N}_2$  at 77 K (Figure 3i). The framework exhibits a certain degree



**FIGURE 3.** Crystal structures of frameworks  $\text{Cu}(\text{FMA})(\text{Pyz})_{0.5}$  (a, b),  $\text{Cu}(\text{FMA})(4,4'\text{-Bipy})_{0.5} \cdot 0.25\text{H}_2\text{O}$  (c, d),  $\text{Cu}(\text{FMA})(4,4'\text{-Bpe})_{0.5} \cdot 0.5 \text{H}_2\text{O}$  (e, f), and  $\text{Cu}(\text{FMA})(4,4'\text{-Bpe})_{0.5}$  (g, h) showing doubly interpenetrated primitive cubic nets and corresponding pore void spaces (condensed (b); pore apertures of  $1.4 \times 1.8 \text{ \AA}^2$  (d) and  $2.0 \times 3.2 \text{ \AA}^2$  (f) (Cu, ball; O, red; H, white), and gas sorption isotherms of  $\text{Cu}(\text{FMA})(4,4'\text{-Bpe})_{0.5}$  at (i) 77 K ( $\text{H}_2$ , green;  $\text{N}_2$ , blue; Ar, magenta; CO, yellow) and (j) 195 K ( $\text{CO}_2$ , red;  $\text{CH}_4$ , pink;  $\text{N}_2$ , blue). Reprinted with permission from ref 32. Copyright 2007 American Chemical Society.





**FIGURE 4.** (a) Reversible open–dense framework transformations in the crystals of  $\text{Zn}(\text{BDC})(4,4'\text{-Bipy})_{0.5}$ , (b) chromatograms of natural gas mixtures and (c) chromatograms of alkane mixtures containing 2-methylbutane (**1**), *n*-pentane (**2**), 2,2-dimethylbutane (**3**), 2-methylpentane (**4**), and *n*-hexane (**5**), obtained on its column ( $S = \text{TCD}$  response). Reprinted with permission from ref 33. Copyright 2006 Wiley-VCH.

of flexibility or dynamics, which is responsible for the hysteresis sorption behaviors of  $\text{CH}_4$  and  $\text{N}_2$  at 196 K.<sup>32</sup>

## 2.2. Tuned Micropores for Recognition of Alkanes.

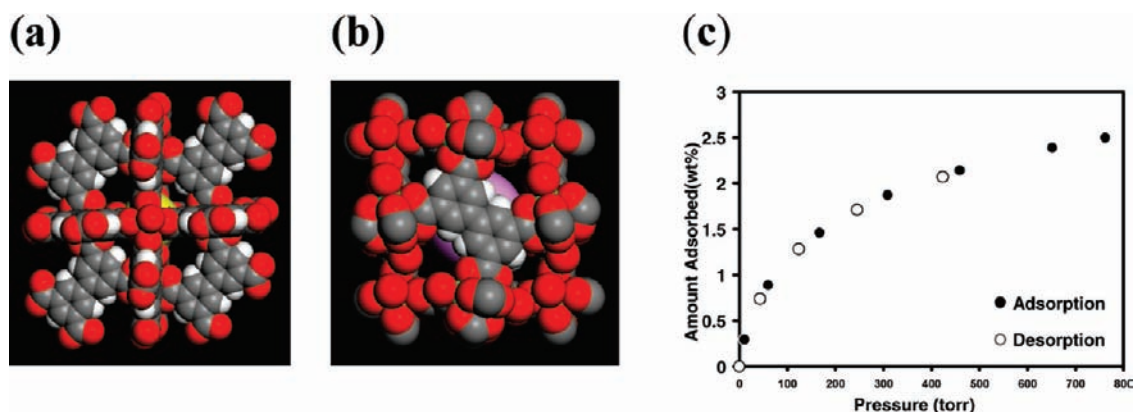
Alkanes are both important raw materials of the chemical industry and the most important fuels of the world economy. Separation of alkanes in the petrochemical industry is based on their different boiling points/vapor pressures by fractional distillation, which is energy consuming. It has been demanding and challenging development of novel materials to separate alkane isomers efficiently. For example, linear alkanes need to be removed from the branched alkanes to boost octane ratings in gasoline. Alkanes with the general formula  $\text{C}_n\text{H}_{2n+2}$  are characteristic of carbon–carbon single bonds in which the carbon atoms are further saturated by hydrogen atoms. Because they have no or slight dipole moments and their interactions with other chemical species are mainly van der Waals interactions, it is very difficult to direct specific interactions for their recognition. By making use of primitive cubic net and double framework interpenetration, we have successfully targeted a microporous MOF,  $\text{Zn}(\text{BDC})(4,4'\text{-Bipy})_{0.5} \cdot (\text{DMF})(\text{H}_2\text{O})_{0.5}$  (BDC = 1,4-benzenedicarboxylate), with one-dimensional micropores of about 4.0 Å to discriminate linear and branched hydrocarbons (Figure 4a, left), and applied it GC separation of hydrocarbon. The micropores of 4.0 Å within  $\text{Zn}(\text{BDC})(4,4'\text{-Bipy})_{0.5}$ , which are slightly larger than the size of methane (3.8 Å), allow pore surface interactions with the linear parts of alkanes. Apparently, the shorter the linear part the alkane isomer has, the weaker its interactions with the MOF  $\text{Zn}(\text{BDC})(4,4'\text{-Bipy})_{0.5}$ ; thus the isomer with the shorter linear part will elute from the GC column first, so natural gas mixtures (Figure 4b), and pentane and hexane isomers (Figure 4c) can be straightforwardly separated in a GC column packed with porous MOF  $\text{Zn}(\text{BDC})(4,4'\text{-Bipy})_{0.5}$ . This is the first example of such microporous MOFs for gas chromatographic separation of small molecules. Another very interesting feature of

this microporous MOF is its dynamic properties exhibiting reversible open–dense framework transformations in the crystals as shown in Figure 4a.<sup>33</sup>

## 3. Functional Sites within Porous MOFs for High Gas Storage and Selective Sensing

Incorporation of specific binding sites within porous MOFs is the key for their functional properties; we thus developed the strategies to immobilize open metal sites, Lewis acidic sites, and Lewis basic pyridyl sites for their recognition of hydrogen, acetylene, metal ions, and anions. The success of these approaches has enabled us to target high hydrogen and acetylene storage materials and realize some porous luminescent materials for the sensing of acetone,  $\text{Cu}^{2+}$ , and  $\text{F}^-$ .

**3.1. Optimized Pore Surfaces and Open-Metal Sites to Enhance  $\text{H}_2$  Uptake.** Although the emerging porous MOFs show promise as hydrogen storage materials, it is a daunting challenge to reach the targeted goals for FreedomCAR hydrogen storage with uptake of 6.0 wt % in 2010 and 9.0 wt % in 2015, specified by the Department of Energy at moderate temperature and pressure. The main issue is that such pores cannot be fully utilized for  $\text{H}_2$  storage at moderate temperatures because of the weak van der Waals interactions between  $\text{H}_2$  and pore surfaces. To enhance their  $\text{H}_2$  uptake, it is necessary to optimize the pore surfaces/curvatures for efficient hydrogen packing. Furthermore, strong sorption sites need to be incorporated into the pores for their stronger interactions with hydrogen molecules to maximize the  $\text{H}_2$  uptake. With these considerations in mind, we have been able to design and synthesize an NbO-type microporous MOF,  $\text{Cu}_2(\text{BPTC})(\text{H}_2\text{O})_2 \cdot (\text{DMF})_3(\text{H}_2\text{O})$ , with two types of micropores of about 4 and 9 Å (Figure 5a,b) and open copper sites for high hydrogen storage at 1 atm and 77 K. Hydrogen sorption studies indicated that the material takes up 2.0 wt %  $\text{H}_2$  when the



**FIGURE 5.** (a) Small pore (yellow sphere) and (b) large pore (purple sphere) in the single crystal structure of  $\text{Cu}_2(\text{BPTC})(\text{H}_2\text{O})_2 \cdot (\text{DMF})_3(\text{H}_2\text{O})$  and (c) hydrogen gas isotherm at 77 K of desolvated microporous material  $\text{Cu}_2(\text{BPTC})$  (C, gray; O, red; Cu, green).

free solvent guests have been removed. More importantly, by further removal of the coordinated water molecules, the created open copper sites significantly increase the hydrogen uptake up to 2.5 wt %, by copper site–hydrogen interactions, highlighting the crucial role of open metal sites for hydrogen storage.<sup>41</sup>

### 3.2. Open Metal Sites within Porous MOFs for Extraordinarily High Acetylene Storage at Room Temperature.

Because of the very explosive nature of acetylene, acetylene storage must be realized at room temperature under pressure of 0.2 MPa (the compression limit for the safe storage of acetylene), so specific binding sites need to be immobilized within porous MOFs for their enhanced interactions with acetylene and thus high acetylene uptake. As shown in Figure 6(I,II), the pore spaces in porous MOFs with large pores and high surface areas are basically not useful for acetylene storage at room temperature and 1 atm because of their weak interactions with acetylene; however, the immobilization of the open  $\text{Cu}^{2+}$  sites into the frameworks HKUST-1 and MOF-505 leads to much higher acetylene uptake than others in which the binding of the open  $\text{Cu}^{2+}$  sites for the acetylene molecules has been exclusively established by high resolution neutron diffraction studies.<sup>42</sup> To immobilize high density open metal sites, we further realized  $\text{Co}_2(\text{DHTP})$  (DHTP = 2,5-dihydroxyterephthalate) as the highest volumetric acetylene storage material ever reported with uptake of  $230 \text{ cm}^3(\text{STP})/\text{cm}^3$  at 295 K and 1 atm.<sup>43</sup> Such high acetylene storage capacity has maximized the safe acetylene storage density of adsorbed acetylene in bulk material up to  $0.27 \text{ g}/\text{cm}^3$ , which is equivalent to the acetylene density at 25.1 MPa. The contribution of the high open  $\text{Co}^{2+}$  site density to the extraordinarily high acetylene storage has also been conclusively established by the high resolution neutron powder diffraction studies on acetylene-loaded  $\text{Co}_2(\text{DHTP})$  with Co–C bonding distance of 2.65 Å and further confirmed by first-principles

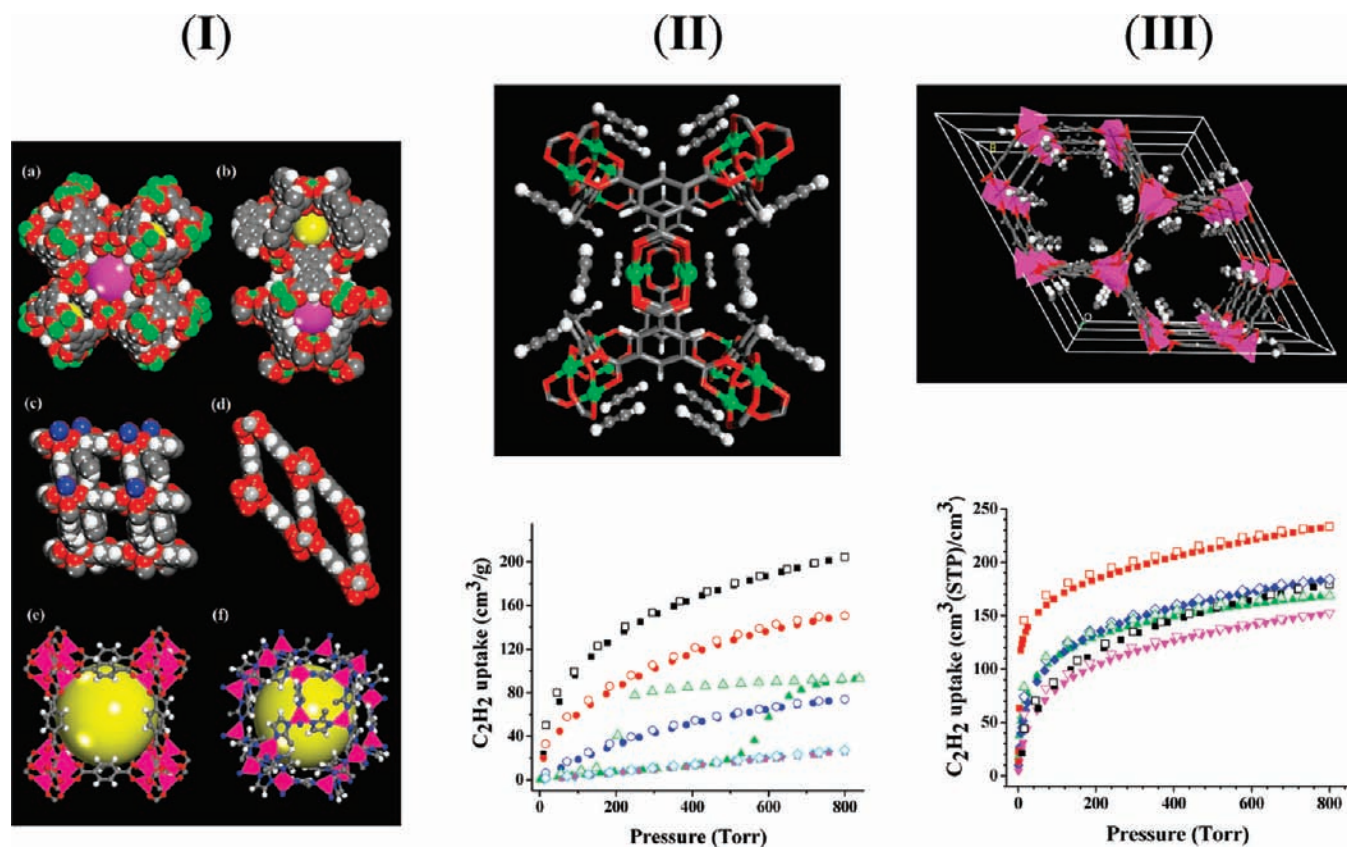
calculation. As shown in Figure 6, such porous MOFs exhibit reversible acetylene adsorption and desorption, which mean that the storage and delivery of acetylene can be easily realized in practical usage. In addition to the open metal sites for their strong interactions with acetylene, hydrogen bonding interactions also play a very important role to enhance their interactions with acetylene. In fact, the first porous MOF for high-density acetylene storage capacity has been realized in an ultramicroporous MOF because of the strong hydrogen bonding interactions between pore surface and acetylene molecules.<sup>44</sup> The extraordinarily high volumetric acetylene storage capacities have featured such microporous hybrid materials as very practical acetylene storage media. Given the fact that acetylene is a very important raw material for various industrial chemicals, consumer products, and oxy-acetylene cutting in metal fabrication shops, the realization of such safe and high-density acetylene storage media will certainly facilitate the safe transportation and wider usage of acetylene in the future.

### 3.3. Luminescent Open Metal Sites for Sensing of Small Molecules.

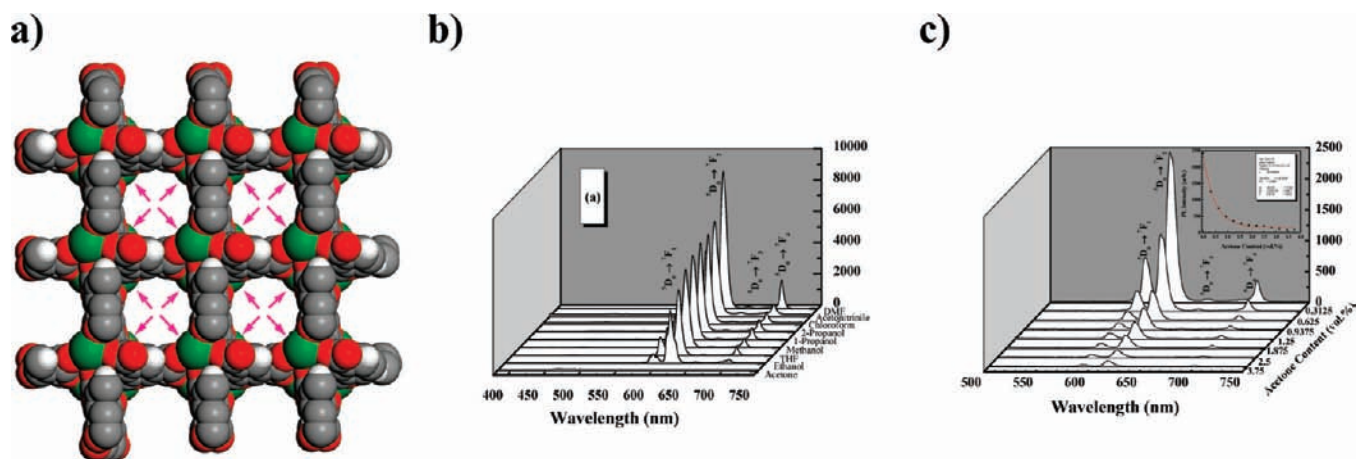
To incorporate luminescent open  $\text{Eu}^{3+}$  sites within a porous MOF  $\text{Eu}(\text{BTC})$  (BTC = benzenetricarboxylate), a rare example of porous MOFs has been developed for the sensing of small molecules (Figure 7). This is attributed to the different response of luminescent open  $\text{Eu}^{3+}$  sites with solvent molecules such as DMF,  $\text{CH}_3\text{CN}$ ,  $\text{CHCl}_3$ , 2-propanol, 1-propanol, methanol, THF, ethanol, and acetone, exhibiting enhancing or quenching luminescent effects (Figure 7b). Specifically, a small amount of acetone can be easily sensed because of its significant luminescence diminishment, which is dependent on its content (Figure 7c).<sup>45</sup>

### 3.4. Lewis Basic Pyridyl Sites within a Luminescent Porous Metal–Organic Framework for Sensing of $\text{Cu}^{2+}$ .

As shown in Figure 8a, we have been able to make use of the preferential binding of lanthanide ions ( $\text{Ln}^{3+}$ ) to carboxylate



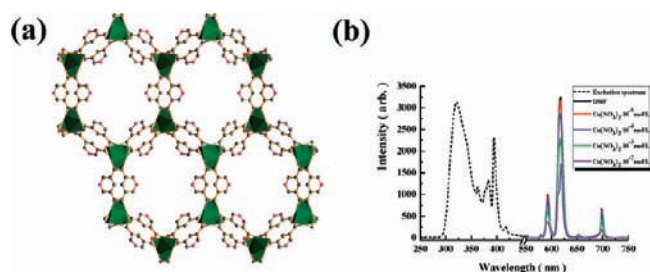
**FIGURE 6.** (I) Single-crystal X-ray structures of (a) HKUST-1, (b) MOF-505, (c) MOF-508, (d) MIL-53, (e) MOF-5, and (f) ZIF-8, showing open  $\text{Cu}^{2+}$  sites (green), 3D frameworks, and corresponding pore/cage sizes. Color scheme: C, gray; H, white; N, blue; O, red; Cu, green; Al, light gray; Zn, pink; (II) the crystal structure of one  $\text{C}_2\text{D}_2$  per Cu-loaded HKUST-1 exhibiting the open  $\text{Cu}^{2+}$  sites for the recognition of acetylene molecules (top) and acetylene adsorption isotherms of microporous MOFs at 295 K (MOF-508 at 290 K); HKUST-1 (black); MOF-505 (red); MOF-508 (green); MIL-53 (blue); MOF-5 (cyan), and ZIF-8 (pink) (bottom); (III) the crystal structure of 0.54  $\text{C}_2\text{D}_2$  per Co-loaded  $\text{Co}_2(\text{DHTP})$  along  $c$  axis exhibiting the high density of adsorbed acetylene molecules in pseudo-one-dimensional arrays (top) and acetylene adsorption isotherms of microporous MOFs at 295 K ( $\text{Co}_2(\text{DHTP})$  (red);  $\text{Mn}_2(\text{DHTP})$  (blue);  $\text{Mg}_2(\text{DHTP})$  (green); HKUST-1 (black);  $\text{Zn}_2(\text{DHTP})$  (pink) (bottom). Reprinted with permission from ref 42. Copyright 2009 American Chemical Society.



**FIGURE 7.** (a) X-ray crystal structure of  $\text{Eu}(\text{BTC})(\text{H}_2\text{O}) \cdot (\text{H}_2\text{O})_{1.5}$  viewed along  $c$  axis, exhibiting one-dimensional channels of about  $6.6 \times 6.6 \text{ \AA}^2$  and uniformly immobilized accessible  $\text{Eu}^{3+}$  sites within the framework shown by the arrows (the free and terminal water molecules are omitted for clarity; Eu, green; O, red; C, gray; H, white), (b) the PL spectra of  $\text{Eu}(\text{BTC})$  introduced into various pure solvent emulsions, and (c) the PL spectra of 1-propanol emulsion of  $\text{Eu}(\text{BTC})$  in the presence of various amounts of acetone solvent (excited at 285 nm; inset, the PL intensity of  $\text{Eu}(\text{BTC})$  versus acetone content). Reprinted with permission from ref 45. Copyright 2007 Wiley-VCH.

oxygen atoms over pyridyl nitrogen atoms in their  $\text{Ln}^{3+}$ –pyridinecarboxylate complexes to immobilize Lewis basic

pyridyl sites into a porous luminescent MOF,  $\text{Eu}(\text{PDC})_{1.5}(\text{DMF}) \cdot (\text{DMF})_{0.5}(\text{H}_2\text{O})_{0.5}$  (**1**, PDC = pyridine-3,5-dicarboxylate). Because



**FIGURE 8.** (a) Single-crystal X-ray structure of  $\text{Eu}(\text{PDC})_{1.5}(\text{DMF}) \cdot (\text{DMF})_{0.5}(\text{H}_2\text{O})_{0.5}$  (**1**, PDC = pyridine-3,5-dicarboxylate) viewed along the  $a$  axis indicating evenly immobilized Lewis basic pyridyl sites (magenta) toward pore centers. Color scheme: C, gray; N, magenta; O, red; Eu, green. Hydrogen atoms and terminal DMF molecules are omitted for clarity. (b) The excitation (dotted) and PL spectra (solid) of **1b** solid activated in different concentrations of  $\text{Cu}(\text{NO}_3)_2$  DMF solution (excited and monitored at 321 and 618 nm, respectively). Reprinted with permission from ref 46. Copyright 2009 Wiley-VCH.

of the differential binding of these Lewis basic pyridyl sites with metal ions, this porous material exhibits a sensing function with respect to metal ions, particularly to  $\text{Cu}^{2+}$ . The addition of  $\text{Cu}^{2+}$  into the microporous  $\text{Eu}(\text{PDC})_{1.5}$  (**1b**) material leads to the decreased luminescent intensity, which is dependent on the concentration of  $\text{Cu}^{2+}$  in the solution because of the quenching effect (Figure 8b), highlighting the potential application of such luminescent porous hybrid materials for the sensing of metal ions.<sup>46</sup>

**3.5. A Luminescent Porous Metal–Organic Framework for Sensing of  $\text{F}^-$ .** In another example of porous luminescent MOFs for the sensing function, terminal methanol molecules were incorporated into a porous luminescent material,  $\text{Tb}(\text{BTC})$  (BTC = benzene-1,3,5-tricarboxylate; Figure 9a) for their differential hydrogen bonding interactions with anions such as  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{CO}_3^{2-}$ , and  $\text{SO}_4^{2-}$ . Because  $\text{F}^-$  has much stronger interactions with the terminal methanol molecules to confine the O–H bond stretching and thus reduce its quenching effect, the addition of  $\text{F}^-$  enhances the luminescence intensity of the material significantly, featuring the bright promise for these kinds of porous luminescent MOFs for the sensing of fluoride anion (Figure 9b).<sup>47</sup>

#### 4. Microporous Mixed-Metal–Organic Frameworks (M'MOFs) for Recognition and Kinetic Molecular Sieving Separation of Small Molecules

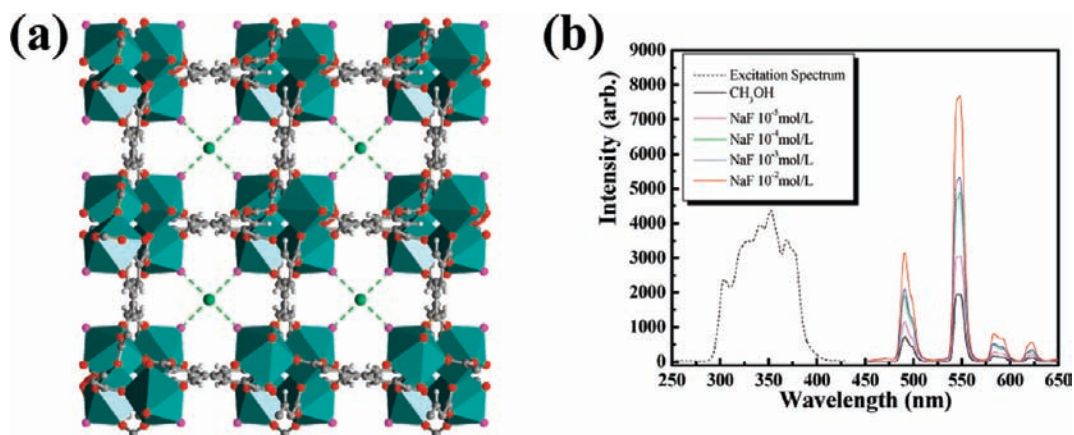
Although open metal sites within porous MOFs have played significant roles for their specific recognition of substrate species and thus functional properties in gas storage, separation, sensing, and catalysis, it is quite challenging to immobilize the open metal sites systematically and rationally into the porous

hybrid materials. In fact, most of the porous MOFs with open metal sites were explored and discovered accidentally. In this regard, the emerging metalloligand or preconstructed building block approach is very promising to immobilize different open metal sites straightforwardly into the porous mixed-metal–organic frameworks (M'MOFs), although it is still at the very early stage.<sup>48–52</sup> Recently, we have made significant progress on this endeavor.<sup>53</sup>

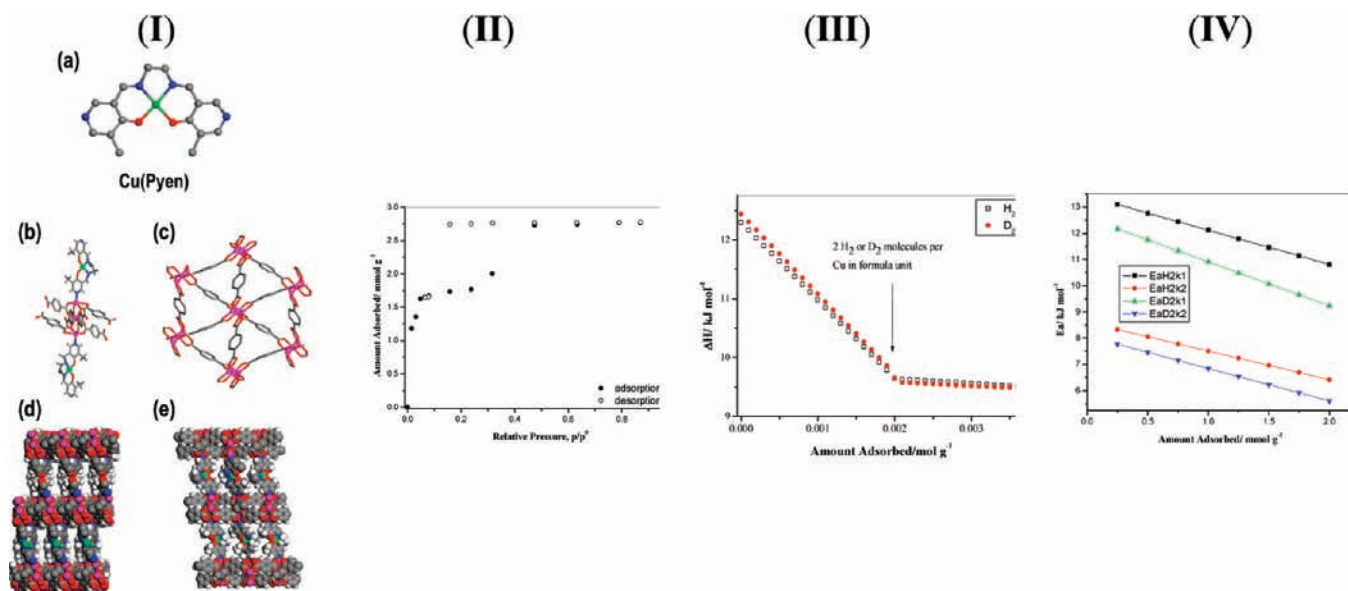
To incorporate a  $\text{Cu}(\text{II})$ –Schiff base complex (Figure 9(I,a)),  $\text{Cu}(\text{Pyen})$  can be readily synthesized by the reaction of  $\text{Cu}(\text{NO}_3)_2$  with the Schiff base, which is formed by the condensed reaction of the corresponding aldehyde with ethylenediamine, as the preconstructed building block containing pyridine terminal sites for their further coordination with metal ions/clusters to assemble into porous M'MOFs. We have successfully synthesized a series of porous M'MOFs with permanent porosity and interesting gas/vapor adsorption properties. One of them is shown in Figure 10. Here the self-assembly of this  $\text{Cu}(\text{Pyen})$  preconstructed building block with  $\text{Zn}(\text{NO}_3)_2$  and  $\text{H}_2\text{BDC}$  ( $\text{H}_2\text{BDC}$  = benzene-1,4-dicarboxylic acid) in DMF at 373 K readily formed  $\text{Zn}_3(\text{BDC})_3[\text{Cu}(\text{Pyen})] \cdot (\text{DMF})_5(\text{H}_2\text{O})_5$  (M'MOF **1**).

The crystal structure of M'MOF **1** is a three-dimensional framework composed of the trinuclear  $\text{Zn}_3(\text{COO})_6$  secondary building units (Figure 10(I,b)). These SBUs are bridged by BDC anions to form the  $3^6$  tessellated  $\text{Zn}_3(\text{BDC})_3$  2-D sheets (Figure 10(I,c)) that are further pillared by the  $\text{Cu}(\text{Pyen})$  to construct a 3D framework. There exist rationally immobilized copper centers within the two types of micropores: curved pores of about  $5.6 \times 12.0 \text{ \AA}^2$  in the direction of the  $c$  crystallographic axis (Figure 10(I,d),  $c$  axis pores) and irregular ultramicropores in the direction of the  $b$  crystallographic axis (Figure 10(I,e),  $b$  axis pores). This gives an array of pores in the  $bc$  crystallographic plane. The copper sites have four of six possible coordination sites bound by Schiff base N and O, so that there are two potential open sites on either side of the  $\text{CuN}_2\text{O}_2$  plane for binding of hydrogen molecules.

The solvent molecules within M'MOF **1** were exchanged with methanol and then removed by activation at 343 K under ultrahigh vacuum ( $10^{-10}$  bar) until no further weight loss occurred prior to gas adsorption studies. The activated M'MOF **1b** exhibits hysteresis adsorption behaviors with respect to methanol and benzene because of the flexibility of the framework (Figure 10(II)). The most interesting and important feature is that two open sites exist per copper atom, which interact with hydrogen molecules very strongly with hydrogen adsorption enthalpy of  $12.29 \pm 0.53 \text{ kJ mol}^{-1}$  at zero coverage (Figure 10(III)), which is much higher than other



**FIGURE 9.** (a) Single-crystal X-ray structure of a luminescent hybrid material Tb(BTC) activated in methanol containing NaF with the model of fluoride (green) at the center of the channel involving its hydrogen bonding interaction with terminal methanol molecules (methanol oxygen, magenta; the methyl group from methanol is omitted for clarity). (b) Excitation (dotted) and PL spectra (solid) of Tb(BTC) solid activated in different concentrations of NaF methanol solution (excited and monitored at 353 and 548 nm, respectively). Reprinted with permission from ref 47. Copyright 2008 American Chemical Society.



**FIGURE 10.** (I) X-ray crystal structure of M'MOF **1** ( $\text{Zn}_3(\text{BDC})_3\text{Cu}(\text{Pyen})$ ) showing (a) Pyen, (b) one trinuclear  $\text{Zn}_3(\text{COO})_6$  secondary building unit, (c) one  $3^6$  tessellated  $\text{Zn}_3(\text{BDC})_3$  2-D sheet that is pillared by the Cu(Pyen) to form a 3-D microporous M'MOF **1** having (d) curved pores of about  $5.6 \times 12.0 \text{ \AA}^2$  along the  $c$  axis and (e) irregular ultramicropores along the  $b$  axis. Color scheme: Zn (magenta), Cu (green), O (red), N (blue), C (gray), H (white). (II) Adsorption isotherm of benzene for M'MOF **1** ( $\text{Zn}_3(\text{BDC})_3\text{Cu}(\text{Pyen})$ ) at 298 K. (III) The variation of enthalpy of adsorption ( $\text{kJ mol}^{-1}$ ) with amount adsorbed ( $\text{mol g}^{-1}$ ) for  $\text{H}_2$  and  $\text{D}_2$  adsorption on M'MOF **1** ( $\text{Zn}_3(\text{BDC})_3\text{Cu}(\text{Pyen})$ ). (IV) The variation of activation energy ( $E_a$ ,  $\text{kJ mol}^{-1}$ ) with amount adsorbed ( $\text{mmol g}^{-1}$ ) for  $\text{H}_2$  and  $\text{D}_2$  adsorption on M'MOF **1** ( $\text{Zn}_3(\text{BDC})_3\text{Cu}(\text{Pyen})$ ). Reprinted with permission from ref 53. Copyright 2008 American Chemical Society.

reported open metal sites for their interactions with hydrogen molecules in porous MOFs. Another very significant feature is the differential adsorption kinetics for  $\text{H}_2$  and  $\text{D}_2$  confined by both open metal sites and ultramicroporosity within the two types of pores in M'MOF **1**. The rate constants for heavier  $\text{D}_2$  were faster and the activation energies slightly lower than the corresponding values for  $\text{H}_2$  kinetics for both components (Figure 10(IV)). This is attributed to quantum effects with the higher zero-point energy for  $\text{H}_2$  giving a higher effective collision cross section than  $\text{D}_2$ , producing a higher

barrier to diffusion along the pores. Such differential adsorption kinetics might be utilized for the kinetic sieving separation of  $\text{H}_2/\text{D}_2$ . This is the first experimental observation of kinetic isotope quantum molecular sieving in such MOF materials.<sup>53</sup>

## 5. Conclusion and Outlook

We have outlined several successful strategies to construct porous MOFs with functional sites for their specific and unique



recognition of small molecules such as hydrogen, acetylene, carbon dioxide, methane, acetone, copper ion, and fluoride, and thus for their applications in gas storage, separation, and sensing. The ability to rationally and systematically tune the micropores has featured the emerging porous MOF materials as very promising media for the separation and purification of small gas molecules, given the fact that some of porous MOFs are highly stable. As established by our recent fixed bed adsorption and breakthrough experiments, gas separation capacities can be enlarged by utilizing higher amounts of MOF materials; it is thus expected that some porous MOFs will be implemented in industrial usage for the separation and purification of small gas molecules in the near future.<sup>54,55</sup> The very high acetylene storage of our reported porous MOFs at room temperature and 1 atm has highlighted the promise of porous MOFs as practical acetylene storage materials. The exploration of porous MOFs for sensing functions is still at a very early stage and will be certainly pursued extensively, particularly with the realization of nanoscale luminescent porous MOFs.<sup>56</sup> The realization of porous mixed-metal–organic frameworks (M'MOFs) with permanent porosity and kinetic molecular sieving separation of D<sub>2</sub>/H<sub>2</sub> has opened the new strategy to construct porous MOFs whose pore or window sizes can be tuned by different organic linkers while pore surfaces can be easily and straightforwardly functionalized by the immobilization of different metal sites and chiral moieties for their applications in gas separation and enantioselective separation. The interactions between the porous MOFs and gas molecules are mainly van der Waals interactions, which can be enhanced by the confined small pores within MOFs. However, such small pore enhancement for their strong interactions with gas molecules is very limited; it is thus very important to immobilize some specific sites such as open metal sites and -NH<sub>2</sub> on the pore surface to direct strong interactions with gas molecules, particularly for high gas storage and separation at moderate temperatures.<sup>57</sup> We are currently developing new porous M'MOFs with different open metal sites and organic functional sites for the separation of O<sub>2</sub>/N<sub>2</sub>, C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub>, and C<sub>2</sub>H<sub>4</sub>/C<sub>2</sub>H<sub>6</sub> and enantioselective separation of some small chiral molecules.

*The authors would like to thank a number of great scientists with whom we have been collaborating and whose names are found in the cited works. We acknowledge funding support from the National Science Foundation (Grant CHE-0718281) and National Nature Science Foundation of China (Grant No. 50928201).*

## BIOGRAPHICAL INFORMATION

**Banglin Chen** was born in Zhejiang, China. He received B.S. (1985) and M.S. (1988) degree in Chemistry from Zhejiang University in China and Ph.D. from National University of Singapore in 2000. He worked with Professors Omar M. Yaghi at University of Michigan, Stephen Lee at Cornell University, and Andrew W. Maverick at Louisiana State University as a postdoctoral fellow during 2000–2003 before joining the University of Texas–Pan American in 2003. He moved to the University of Texas at San Antonio in August 2009 as the Associate Professor of Chemistry.

**Shengchang Xiang** was born in Fujian, China (1972), and received his Ph.D. degree in physical chemistry in 2003 from Fuzhou University. He joined Prof. Xin-Tao Wu's Group in Fujian Institute of Research on the structures of Matter, Chinese Academy of Sciences, as a postdoctoral Fellow and then associate professor (2003–2007). He is now working at the University of Texas at San Antonio as a postdoctoral Fellow. His work is focused on multifunctional organic–inorganic hybrid materials.

**Guodong Qian** was born in Zhejiang, China. He received his bachelor's (1988) and master's (1992) degrees in Materials Science from Zhejiang University in China. He joined the Materials Department of Zhejiang University after obtaining his Ph.D. degree from Zhejiang University in 1997. He was promoted to associate professor and full professor in 1999 and 2002, respectively.

## FOOTNOTES

\*To whom correspondence should be addressed. E-mail addresses: banglin.chen@utsa.edu; gdqian@zju.edu.cn. Fax (B.C.): 210-458-7428. Fax (G.Q.): (+086)571-879-51234.

## REFERENCES

- Hoskins, B. F.; Robson, R. Infinite polymeric frameworks consisting of three dimensionally linked rod-like segments. *J. Am. Chem. Soc.* **1989**, *111*, 5962–5964.
- Kondo, M.; Yoshitomi, T.; Seki, K.; Matsuzaka, H.; Kitagawa, S. Three-dimensional framework with channeling cavities for small molecules: {[M<sub>2</sub>(4,4'-bpy)<sub>3</sub>(NO<sub>3</sub>)<sub>4</sub>] · xH<sub>2</sub>O}<sub>n</sub> (M = Co, Ni, Zn). *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1725–1727.
- Li, H.; Eddaoudi, M.; O'Keeffe, M.; Yaghi, M. Design and synthesis of an exceptionally stable and highly porous metal-organic framework. *Nature* **1999**, *402*, 276–279.
- Chui, S. S.-Y.; Lo, S. M.-F.; Charmant, J. P. H.; Orpen, A. G.; Williams, I. D. A chemically functionalizable nanoporous material [Cu<sub>3</sub>(TMA)<sub>2</sub>(H<sub>2</sub>O)<sub>3</sub>]<sub>n</sub>. *Science* **1999**, *283*, 1148–1150.
- Chen, B.; Eddaoudi, M.; Hyde, S. T.; O'Keeffe, M.; Yaghi, O. M. Interwoven metal-organic framework on a periodic minimal surface with extra-large pores. *Science* **2001**, *291*, 1021–1023.
- Ferey, G. Materials science: The simplicity of complexity - Rational design of giant pores. *Science* **2001**, *291*, 994–995.
- Seo, J. S.; Whang, D.; Lee, H.; Jun, S. I.; Oh, J.; Jeon, Y. J.; Kim, K. A homochiral metal-organic porous material for enantioselective separation and catalysis. *Nature* **2000**, *404*, 982–986.
- Eddaoudi, M.; Kim, J.; Rosi, N.; Vodak, D.; Wachter, J.; O'Keeffe, M.; Yaghi, O. M. Systematic design of pore size and functionality in isorecticular MOFs and their application in methane storage. *Science* **2002**, *295*, 469–472.
- Hu, A.; Ngo, H. L.; Lin, W. Chiral porous hybrid solids for practical heterogeneous asymmetric hydrogenation of aromatic ketones. *J. Am. Chem. Soc.* **2003**, *125*, 11490–11491.
- Zhao, X.; Xiao, B.; Fletcher, A. J.; Thomas, K. M.; Bradshaw, D.; Rosseinsky, M. J. Hysteretic adsorption and desorption of hydrogen by nanoporous metal-organic frameworks. *Science* **2004**, *306*, 1012–1015.

- 11 Ferey, G.; Mellot-Draznieks, C.; Serre, C.; Millange, F.; Dutour, J.; Surble, S.; Margiolaki, I. A chromium terephthalate-based solid with unusually large pore volumes and surface area. *Science* **2005**, *309*, 2040–2042.
- 12 Park, Y. K.; Choi, S. B.; Kim, H.; Kim, K.; Won, B.-H.; Choi, K.; Choi, J.-S.; Ahn, W.-S.; Won, N.; Kim, S.; Jung, D. H.; Choi, S.-H.; Kim, G.-H.; Cha, S.-S.; Jhon, Y. H.; Yang, J. K.; Kim, J. Crystal structure and guest uptake of a mesoporous metal-organic framework containing cages of 3.9 and 4.7 nm in diameter. *Angew. Chem., Int. Ed.* **2007**, *46*, 8230–8233.
- 13 Serre, C.; Mellot-Draznieks, C.; Surble, S.; Audebrand, N.; Filinchuk, Y.; Ferey, G. Role of solvent-host interactions that lead to very large swelling of hybrid frameworks. *Science* **2007**, *315*, 1828–1831.
- 14 Horike, S.; Shimomura, S.; Kitagawa, S. Soft porous crystals. *Nat. Chem.* **2009**, *1*, 695–704.
- 15 Long, J. R.; Yaghi, O. M. The pervasive chemistry of metal-organic frameworks. *Chem. Soc. Rev.* **2009**, *38*, 1213–1214.
- 16 Lin, W.; Zhou, H.-C. MOFs, What are they good for? Presented at the MOF symposium of 235th ACS National Meeting, New Orleans, LA, United States, April 6–10, 2008.
- 17 Chen, S.; Zhang, J.; Wu, T.; Feng, P.; Bu, X. Multiroute synthesis of porous anionic frameworks and size-tunable extraframework organic cation-controlled gas sorption properties. *J. Am. Chem. Soc.* **2009**, *131*, 16027–16029.
- 18 Lin, X.; Telepeni, I.; Blake, A. J.; Dailly, A.; Brown, C. M.; Simmons, J. M.; Zoppi, M.; Walker, G. S.; Thomas, K. M.; Mays, T. J.; Hubberstey, P.; Champness, N. R.; Schroder, M. High capacity hydrogen adsorption in Cu(II) tetracarboxylate framework materials: The role of pore size, ligand functionalization, and exposed metal sites. *J. Am. Chem. Soc.* **2009**, *131*, 2159–2171.
- 19 Zhang, J.-P.; Chen, X.-M. Optimized acetylene/carbon dioxide sorption in a dynamic porous crystal. *J. Am. Chem. Soc.* **2009**, *131*, 5516–5521.
- 20 Ma, S.; Sun, D.; Yuan, D.; Wang, X.-S.; Zhou, H.-C. Preparation and gas adsorption studies of three mesh-adjustable molecular sieves with a common structure. *J. Am. Chem. Soc.* **2009**, *131*, 6445–6451.
- 21 Mulfort, K. L.; Farha, O. K.; Stern, C. L.; Sarjeant, A. A.; Hupp, J. T. Post-synthesis alkoxide formation within metal–organic framework materials: A strategy for incorporating highly coordinatively unsaturated metal ions. *J. Am. Chem. Soc.* **2009**, *131*, 3866–3868.
- 22 Choi, H.-S.; Suh, M. P. Highly selective CO<sub>2</sub> capture in flexible 3D coordination polymer networks. *Angew. Chem., Int. Ed.* **2009**, *48*, 6865–6869.
- 23 Fang, Q.-R.; Zhu, G.-S.; Jin, Z.; Ji, Y.-Y.; Ye, J.-W.; Xue, M.; Yang, H.; Wang, Y.; Qiu, S.-L. Mesoporous metal-organic framework with rare etb topology for hydrogen storage and dye assembly. *Angew. Chem., Int. Ed.* **2007**, *46*, 6638–6642.
- 24 Lan, A.; Li, K.; Wu, H.; Olson, D. H.; Emge, T. J.; Ki, W.; Hong, M.; Li, J. A luminescent microporous metal-organic framework for the fast and reversible detection of high explosives. *Angew. Chem., Int. Ed.* **2009**, *48*, 2334–2338.
- 25 Bradshaw, D.; Claridge, J. B.; Cussen, E. J.; Prior, T. J.; Rosseinsky, M. J. Design, chirality, and flexibility in nanoporous molecule-based materials. *Acc. Chem. Res.* **2005**, *38*, 273–282.
- 26 Nouar, F.; Eubank, J. F.; Bousquet, T.; Wojtas, L.; Zaworotko, M. J.; 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.
- 27 An, J.; Geib, S. J.; Rosi, N. L. High and selective CO<sub>2</sub> uptake in a cobalt adeninate metal–organic framework exhibiting pyrimidine- and amino-decorated pores. *J. Am. Chem. Soc.* **2010**, *132*, 38–39.
- 28 Sumida, K.; Hill, M. R.; Horike, S.; Dailly, A.; Long, J. R. Synthesis and hydrogen storage properties of Be<sub>12</sub>(OH)<sub>12</sub>(1,3,5-benzenetribenzoate)<sub>4</sub>. *J. Am. Chem. Soc.* **2009**, *131*, 15120–15121.
- 29 Wu, H.; Zhou, W.; Yildirim, T. High-capacity methane storage in metal–organic frameworks M<sub>2</sub>(dhtp): The important role of open metal sites. *J. Am. Chem. Soc.* **2009**, *131*, 4995–5000.
- 30 Dybtsev, D. N.; Chun, H.; Kim, K. Rigid and flexible: A highly porous metal-organic framework with unusual guest-dependent dynamic behavior. *Angew. Chem., Int. Ed.* **2004**, *43*, 5033–5036.
- 31 Ma, B.-Q.; Mulfort, K. L.; Hupp, J. T. Microporous pillared paddle-wheel frameworks based on mixed-ligand coordination of zinc ions. *Inorg. Chem.* **2005**, *44*, 4912–4914.
- 32 Chen, B.; Ma, S.; Zapata, F.; Fronczek, F. R.; Lobkovsky, E. B.; Zhou, H.-C. Rationally designed micropores within a porous metal–organic framework for selective sorption of gas molecules. *Inorg. Chem.* **2007**, *46*, 1233–1236.
- 33 Chen, B.; Liang, C.; Yang, J.; Contreras, D. S.; Clancy, Y. L.; Lobkovsky, E. B.; Yaghi, O. M.; Dai, S. A Microporous metal-organic framework for gas chromatographic separation of alkanes. *Angew. Chem., Int. Ed.* **2006**, *45*, 1390–1393.
- 34 Chen, B.; Ma, S.; Zapata, F.; Lobkovsky, E. B.; Yang, J. Hydrogen adsorption in an interpenetrated dynamic metal–organic framework. *Inorg. Chem.* **2006**, *45*, 5718–5720.
- 35 Chen, B.; Fronczek, F. R.; Courtney, B. H.; Zapata, F. α-Po nets of copper(II)-*trans*-1,4-cyclohexanedicarboxylate frameworks based on a paddle-wheel building block and its enlarged dimer. *Cryst. Growth Des.* **2006**, *6*, 825–828.
- 36 Chen, B.; Ma, S.; Hurtado, E. J.; Lobkovsky, E. B.; Zhou, H.-C. A triply interpenetrated microporous metal–organic framework for selective sorption of gas molecules. *Inorg. Chem.* **2007**, *46*, 8490–8492.
- 37 Chen, B.; Ji, Y.; Xue, M.; Fronczek, F. R.; Hurtado, E. J.; Mondal, J. U.; Liang, C.; Dai, S. Metal–organic framework with rationally tuned micropores for selective adsorption of water over methanol. *Inorg. Chem.* **2008**, *47*, 5543–5545.
- 38 Xue, M.; Ma, S.; Jin, Z.; Schaffino, R. M.; Zhu, G.-S.; Lobkovsky, E. B.; Qiu, S.-L.; Chen, B. Robust metal–organic framework enforced by triple-framework interpenetration exhibiting high H<sub>2</sub> storage density. *Inorg. Chem.* **2008**, *47*, 6825–6828.
- 39 Chen, B.; Ma, S.; Hurtado, E. J.; Lobkovsky, E. B.; Liang, C.; Zhu, H.; Dai, S. Selective gas sorption within a dynamic metal–organic framework. *Inorg. Chem.* **2007**, *46*, 8705–8709.
- 40 Chen, Z.; Xiang, S.; Zhao, D.; Chen, B. Reversible two-dimensional-three dimensional framework transformation within a prototype metal–organic framework. *Cryst. Growth Des.* **2009**, *9*, 5293–5296.
- 41 Chen, B.; Ockwig, N. W.; Millward, A. R.; Contreras, D. S.; Yaghi, O. M. High H<sub>2</sub> adsorption in a microporous metal-organic framework with open metal sites. *Angew. Chem., Int. Ed.* **2005**, *44*, 4745–4749.
- 42 Xiang, S.; Zhou, W.; Gallegos, J. M.; Liu, Y.; Chen, B. Exceptionally high acetylene uptake in a microporous metal–organic framework with open metal sites. *J. Am. Chem. Soc.* **2009**, *131*, 12415–12419.
- 43 Xiang, S.; Zhou, W.; Zhang, Z.; Liu, Y.; Chen, B. Open metal sites within isostructural metal-organic frameworks for differential recognition of acetylene and extraordinarily high acetylene storage at room temperature. *Angew. Chem., Int. Ed.* **2010**, *49*, DOI: 10.1002/anie.201000094.
- 44 Matsuda, R.; Kitaura, R.; Kitagawa, S.; Kubota, Y.; Belosludov, R. V.; Kobayashi, T. C.; Sakamoto, H.; Chiba, T.; Takata, M.; Kawazoe, Y.; Mita, Y. Highly controlled acetylene accommodation in a metal-organic microporous material. *Nature* **2005**, *436*, 238.
- 45 Chen, B.; Yang, Y.; Zapata, F.; Lin, G.; Qian, G.; Lobkovsky, E. B. Luminescent open metal sites within a metal-organic framework for sensing of small molecules. *Adv. Mater.* **2007**, *19*, 1693–1696.
- 46 Chen, B.; Wang, L.; Xiao, Y.; Fronczek, F. R.; Xue, M.; Cui, Y.; Qian, G. A luminescent metal-organic framework with Lewis basic pyridyl sites for sensing of metal ions. *Angew. Chem., Int. Ed.* **2009**, *48*, 500–503.
- 47 Chen, B.; Wang, L.; Zapata, F.; Qian, G.; Lobkovsky, E. B. A luminescent microporous metal–organic framework for the recognition and sensing of anions. *J. Am. Chem. Soc.* **2008**, *130*, 6718–6719.
- 48 Kitaura, R.; Onoyama, G.; Sakamoto, H.; Matsuda, R.; Noro, S.; Kitagawa, S. Immobilization of a metallo Schiff base into a microporous coordination polymer. *Angew. Chem., Int. Ed.* **2004**, *43*, 2684–2687.
- 49 Chen, B.; Fronczek, F. R.; Maverick, A. W. Porous Cu–Cd mixed-metal–organic frameworks constructed from Cu(Pyac)<sub>2</sub>[bis(3-(4-pyridyl)pentane-2,4-dionato)copper(II)]. *Inorg. Chem.* **2004**, *43*, 8209–8211.
- 50 Cho, S.-H.; Ma, B.; Nguyen, S. T.; Hupp, J. T.; Albrecht-Schmitt, T. E. A metal-organic framework material that functions as an enantioselective catalyst for olefin epoxidation. *Chem. Commun.* **2006**, 2563–2565.
- 51 Sakamoto, H.; Matsuda, R.; Bureekaew, S.; Tanaka, D.; Kitagawa, S. A porous coordination polymer with accessible metal sites and its complementary coordination action. *Chem.—Eur. J.* **2009**, *15*, 4985–4989.
- 52 Xie, Z.; Ma, L.; de Krafft, K. E.; Jin, A.; Lin, W. Porous phosphorescent coordination polymers for oxygen sensing. *J. Am. Chem. Soc.* **2010**, *132*, 922–923.
- 53 Chen, B.; Zhao, X.; Putkham, A.; Hong, K.; Lobkovsky, E. B.; Hurtado, E. J.; Fletcher, A. J.; Thomas, K. M. Surface and quantum interactions for H<sub>2</sub> confined in metal–organic framework pores. *J. Am. Chem. Soc.* **2008**, *130*, 6411–6423.
- 54 Bastin, L.; Barcia, P. S.; Hurtado, E. J.; Silva, J. A. C.; Rodrigues, A. E.; Chen, B. A microporous metal–organic framework for separation of CO<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/CH<sub>4</sub> by fixed-bed adsorption. *J. Phys. Chem. C* **2008**, *112*, 1575–1581.
- 55 Barcia, P. S.; Zapata, F.; Silva, J. A. C.; Rodrigues, A. E.; Chen, B. Kinetic separation of hexane isomers by fixed-bed adsorption with a microporous metal–organic framework. *J. Phys. Chem. B* **2007**, *111*, 6101–6103.
- 56 Lin, W.; Rieter, J. W.; Taylor, K. M. L. Modular synthesis of functional nanoscale coordination polymers. *Angew. Chem., Int. Ed.* **2009**, *48*, 650–658.
- 57 Thomas, K. M. Adsorption and desorption of hydrogen on metal-organic framework materials for storage applications: comparison with other nanoporous materials. *Dalton Trans.* **2009**, 1487–1505.