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# Rationally Designed Micropores within a Metal–Organic Framework for Selective Sorption of Gas Molecules

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A microporous metal–organic framework, MOF, Cu(FMA)(4,4'-Bpe)$_{0.5}$ (**3a**, FMA = fumarate; 4,4'-Bpe = 4,4'-Bpe = *trans*-bis(4-pyridyl)ethylene) was rationally designed from a primitive cubic net whose pores are tuned by double framework interpenetration. With pore cavities of about 3.6 Å, which are interconnected by pore windows of 2.0 × 3.2 Å, **3a** shows highly selective sorption behaviors of gas molecules.

## Introduction

It has been challenging to rationally design and tune micropores of porous materials for their selective sorption.[1] As their selective sorption behaviors are mainly determined by size-exclusive effects in which smaller molecules can go through the microporous channels while larger substrates are blocked, the exact control of the micropores is of significant importance for their practical applications in gas separation and purification. In fact, the breakthrough on the tunable pores of Molecular Gate adsorbent has initiated industrial innovation for the economical $N_2$ and $CO_2$ removal.[2]

Microporous metal−organic frameworks (MOFs)[3] have been rapidly emerging as one unique type of porous material due to their potential applications in gas storage,[4] separation,[5] and catalysis.[6] The amenability to design, extraordinary permanent porosity, and dynamics are characteristic of such porous materials, leading to some porous materials superior to traditional inorganic zeolite materials. Although extensive efforts have been pursued to search for microporous MOFs for selective sorption of gas molecules, only a few examples have been reported which were discovered accidentally.[7] Recently, we have been focusing on the rational design strategies to tune micropores for their highly selective sorption of small molecules. Initiated by the work of Seki,[8a] Zaworotko,[8d] Kim,[8g] and others who have incorporated a paddle-wheel cluster $M_2(COO)_4$ with a bicarboxylate and a bidentate pillar linker to construct 3D porous primitive cubic

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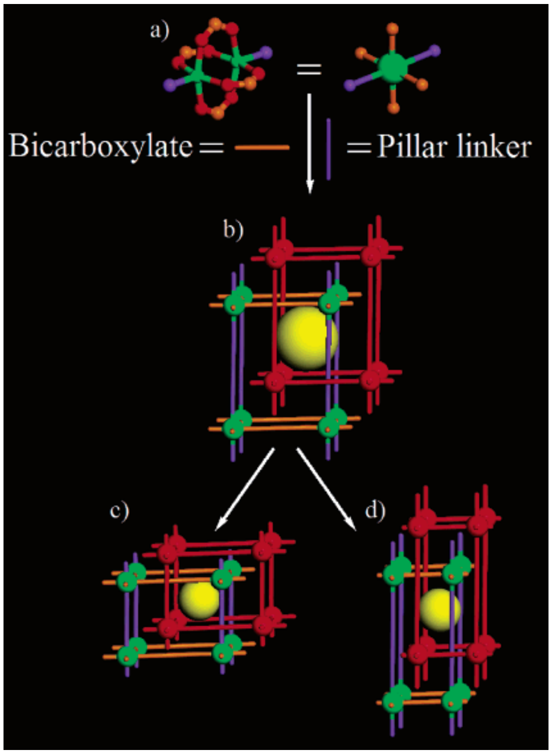
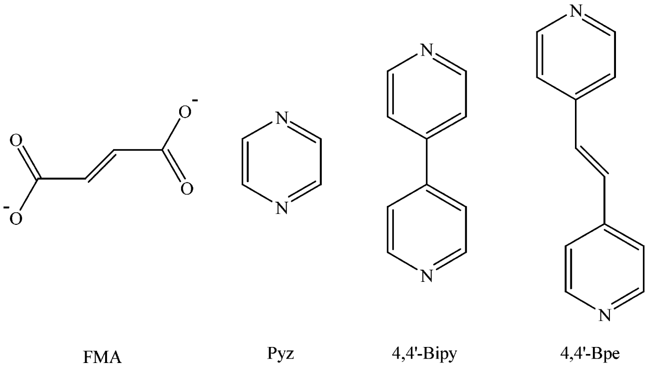
**Scheme 1** [a]



[a] Schematic illustration of (a), a paddle-wheel $M_2(COO)_4$ 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), a shorter pillar organic linker, and (d), a shorter bicarboxylate organic linker.

MOFs $M(R)(L)_{0.5}\cdot G_x$ ($M^{2+}$ = $Cu^{2+}$ and $Zn^{2+}$, R = bicarboxylate linker, L = bidentate pillar linker, G = guest molecules),[8] we have successfully tuned the micropores to about 4.0 × 4.0 Å in $Zn(BDC)(4,4'\text{-}Bipy)_{0.5}$ by making use of framework interpenetration and have applied the first microporous MOF into the gas chromatographic separation of alkanes.[5e] For separation and purification of smaller gas molecules such as $H_2$, Ar, $N_2$, and $CO_2$, such micropores need to be further narrowed down, which we believe can be simply and readily fulfilled by the different combination of bicarboxylate R and bidentate pillar linker L and/or multiple framework interpenetration. As illustrated in Scheme 1, the pore void space within a doubly interpenetrated primitive cubic framework (b) can be easily tuned and reduced by incorporating a shorter pillar linker L and a shorter bicarboxylate R to form smaller pore void space in (c) and (d), respectively. Herein, we report the rational design and synthesis of three primitive cubic MOFs, $Cu(FMA)(Pyz)_{0.5}$ (**1**), $Cu(FMA)(4,4'\text{-}Bipy)_{0.5}\cdot 0.25H_2O$ (**2**),[8a] and $Cu(FMA)(4,4'\text{-}Bpe)_{0.5}\cdot 0.5H_2O$ (**3**), which are self-assembled by the incorporation of fumarate (FMA) with pillar linker pyrazine (Pyz), 4,4-bipyridine(4,4’-Bipy), and 4,4'-Bpe = *trans*-bis(4-pyridyl)ethylene(4,4’-Bpe), respectively. As revealed in their single X-ray crystal structures and sorption studies, the pore void spaces in these MOFs are systematically tuned simply by changing the pillar linker L in which a microporous MOF **3** is rationally designed and constructed for its selective sorption of gas molecules.



## Experimental Section

**Materials and Methods:** All reagents and solvents employed were commercially available and used as supplied without further purification. TGA data were obtained on an TGA G500 V5.3 Build 171 instrument with a heating rate of 5 °C/min under a $N_2$ atmosphere. Powder XRD patterns were obtained with a Scintag X1 powder diffractometer system using Kα radiation with a variable divergent slit and a solid-state detector. The routine power was 1400 W (40 kV, 35 mA). Low-background quartz XRD slides (Gem Depot, Inc., Pittsburgh, PA) were used. For analyses, powder samples were dispersed on glass slides.

**MOF 3:** A solution of $Cu(NO_3)_2\cdot 2.5H_2O$ (0.0663 g, 0.285 mmol), $H_2FMA$ (0.0331 g, 0.285 mmol), and 4,4’-Bpe (0.0260 g, 0.143 mmol) in $H_2O$ (25 mL) in a 30 mL vial was heated at 100 °C for 24 h to form blue-green, block-shaped crystals (41 mg, 52%). Anal. Calcd for $Cu(C_4H_2O_4)(C_{12}H_{10}N_2)_{0.5}\cdot 0.5H_2O$: C,

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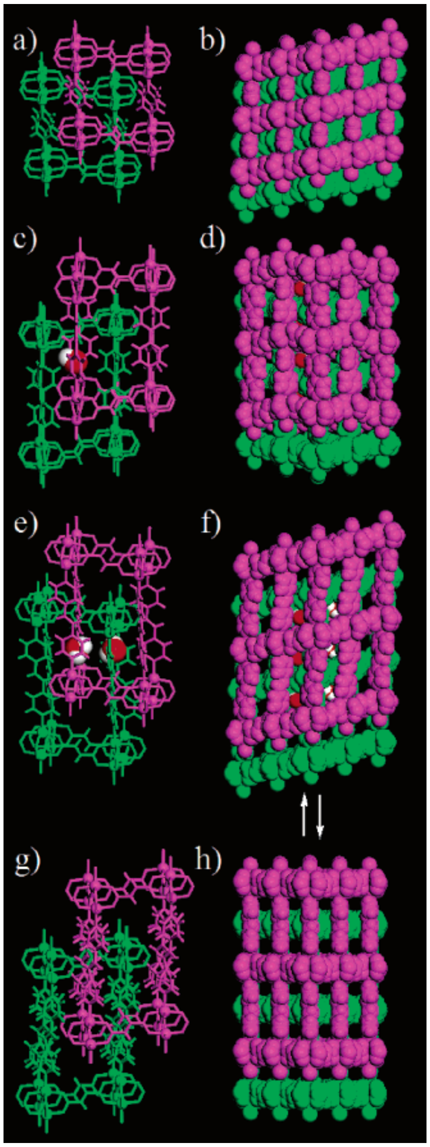

**Figure 1.** Crystal structures of frameworks **1** (a, b), **2** (c, d), **3** (e, f), and **3a** (g, h) showing doubly interpenetrated primitive cubic nets and corresponding pore void spaces. For (h), 4,4'-Bpe pillar linkers are disordered, and only one of the possible conformations is shown (Cu, ball; O, red; H, white).

43.24; H, 2.90; N, 5.04. Found: C, 43.33, H, 2.74; N, 5.10%. MOFs **1**−**2** were synthesized similarly. **MOF 3a**: Sample of MOF **3** was heated at 150 °C in vacuum for 24 h to get MOF **3a**. TGA indicates that there is no further weight loss.

**Single-Crystal X-ray Crystallography:** Intensity data for MOFs **1**, **2**, and **3a** were collected using a Bruker X8 APEX II diffractometer (Mo radiation) in a cold nitrogen stream. Data collection and reduction were done using the Bruker Apex2 software package. Intensity data for MOF **3** were collected using graphite-monochromated Mo radiation on a Nonius KappaCCD diffractometer fitted with an Oxford Cryostream cooler. Data reduction included absorption corrections by the multiscan method. Structures were solved by direct methods and refined by full-matrix least squares, using SHELXL97. All non-hydrogen atoms were refined anisotropically. CCDC-616534 (MOF **1**), CCDC-616535 (MOF **2**), and CCDC-616536 (MOF **3**) contain the supplementary crystallographic data for this paper. The atomic coordinates for this structure have been deposited with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK or at www.ccdc.cam.ac.uk/conts/retrieving.html.

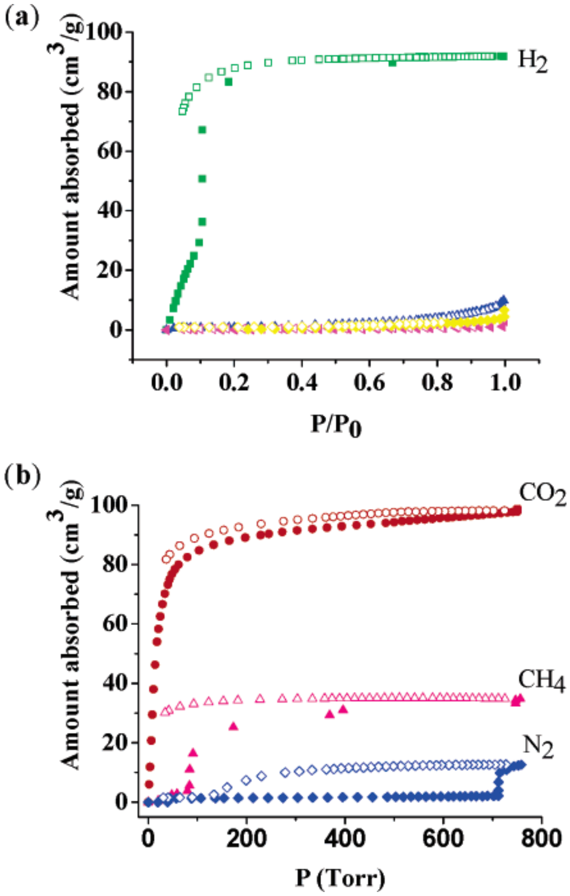

**Figure 2.** Gas sorption isotherms of **3a** at (a) 77 K ($H_2$, green; $N_2$, blue; Ar, magenta; CO, yellow) and (b) 195 K ($CO_2$, red; $CH_4$, pink; $N_2$, blue).

**Gas Sorption Measurements:** A Beckman Coulter SA3100 surface area analyzer was used to measure gas adsorption. In order to remove guest solvent molecules in the framework, the fresh sample soaked in methanol was filtered and vacuumed at 150 °C overnight. Before the measurement, the sample was vacuumed again by using the "outgas" function of the surface area analyzer for 2 h at 150 °C. A sample of 90.0 mg was used for the sorption measurement and was maintained at 77 K with liquid nitrogen and at 195 K with an acetone/dry ice slush.

## Results and Discussion

All three MOFs were synthesized by hydrothermal reactions of $Cu(NO_3)_2 \cdot 2.5H_2O$ with the corresponding organic linkers at 100 °C for 1 day as blue, block-shaped crystals. As expected, the frameworks of MOFs **1**−**3** contain paddle-wheel binuclear $Cu_2$ units which are bridged by FMA dianions to form a distorted 2D square grid $\{Cu_2(FMA)_2\}$. These 2D square grids are further pillared by pyrazine, 4,4'-bipyridine, and *trans*-bis(4-pyridyl)ethylene occupying the axial sites of the $Cu_2$ paddle wheels to form 3D MOFs **1**−**3**, respectively (Figure 1). The topologies of **1**−**3** can be best described as an elongated primitive cubic (α-Po) net. The overall structures are a pair of identical α-Po nets which are mutually interpenetrated with each other to form 2-fold interpenetrated 3D frameworks. It is of particular interest to point out that the pore void spaces in these MOFs are systematically tuned simply by changing the pillar linkers. Crystal packing indicates that **1** is a nonporous condensed framework (Figure 1b), while both **2** and **3** contain pore void space of about 3.6 Å diameter to encapsulate one and two water molecules, respectively, per doubly interpenetrated framework unit (Figure 1c and e). The pore void spaces are disconnected and blocked by the small pore apertures of about 1.4 × 1.8 Å in **2**. However, the pore apertures are enlarged by incorporating longer pillar linker *trans*-bis(4-pyridyl)ethylene in **3** instead of 4,4'-bipyridine as in **2**; thus, a rationally designed microporous MOF **3** with 1D channels of about 2.0 × 3.2 Å to interconnect the pore cavities (Figure 1f), taken into account the van der Waals radius, is readily constructed.[9]

The dehydrated **2** and **3** are thermally stable up to 250 °C, as shown in their TGA studies, but they still keep crystalline forms; thus, the X-ray crystal structure of dehydrated **3** (Cu(FMA)(4,4'-Bpe)$_{0.5}$, **3a**) was characterized. The X-ray crystal structure of **3a** shows that the framework keeps the same connectivity, which is slightly shifted. Unlike desolvated Zn(BDC)(4,4'-Bipy)$_{0.5}$, which is significantly compressed and condensed, **3a** is slightly expanded. The volume per formula unit increases from 1153.4 (**3**) to 1174.78 Å$^3$ (**3a**), a 1.9% expansion; thus, the pores become slightly larger (Figure 1h). Single X-ray and PXRD studies (Supporting Information) indicate that transformations between **3** and **3a** are reversible.

Sorption studies show that dehydrated **2** does not take up both $H_2$ and $N_2$ at 77 K, obviously because of the small pore apertures of 1.4 × 1.8 Å that block the entrance of gas molecules. However, **3a** can take up a significant amount of 91.8 cm$^3$/g (STP) or 0.8 wt % $H_2$ at 1 atm and 77 K, exhibiting highly selective sorption to entrap $H_2$ (2.8 Å) and to exclude Ar (3.4 Å), $N_2$ (3.64 Å), and CO (3.76 Å) (Figure 2a).[10] It needs to be noted that, at a higher temperature of 195 K, the pore apertures are enlarged under certain pressures; thus, **3a** absorbs a small amount of $N_2$ (Figure 2b). Such aperture expansion might be attributed to the framework dynamics in which higher temperature and pressure will facilitate the entrance of guest molecules through the pore channels.[5e] MOF **3a** shows selective sorption of $CO_2$ (3.3 Å) over $CH_4$ (3.8 Å) at 195 K (Figure 2b).[10] The different hysteretic sorption behaviors with respect to $H_2$, $N_2$, $CO_2$, and $CH_4$ are due to their different van der Waals interactions with the host framework.[8e]

In summary, we have successfully synthesized a rare example of porous MOFs with rationally designed micropores for selective gas sorption. It is worth noting that such microporous materials are of special interest for their potential applications for the separation and purification of gas molecules by the pressure swing adsorption (PSA) technique.[11] Further research on rational design and construction of a series of tunable microporous MOFs for PSA separation of gas molecules is currently underway.

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**Supporting Information Available:** X-ray crystallographic data of **3a**, PXRD pattern, and TGA spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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