

## A Triply Interpenetrated Microporous Metal–Organic Framework for Selective Sorption of Gas Molecules

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A microporous metal–organic framework  $Zn(ADC)(4,4'-Bpe)_{0.5} \cdot xG$  [1; ADC = 4,4'-azobenzene dicarboxylate, 4,4'-Bpe = *trans*-bis-(4-pyridyl)ethylene, G = guest molecules] with a triply interpenetrative primitive cubic net was synthesized and characterized. With pores of about  $3.4 \times 3.4 \text{ \AA}$ , the activated **1a** exhibits highly selective sorption behavior toward  $H_2/N_2$ ,  $H_2/CO$ , and  $CO_2/CH_4$ .

The tuning of micropores within porous materials is of great importance for their application in the separation of small molecules, as exemplified in Molecular Gate adsorbent whose pores are tunable for the economical nitrogen and carbon dioxide removal.<sup>1</sup> During the last 2 decades, microporous metal–organic frameworks (MOFs) have been rapidly emerging as a new type of microporous materials for their functional gas storage and separation capacities. Unlike traditional porous zeolite materials whose pores are confined by tetrahedral oxide skeletons and thus are difficult to tune, the pores within MOFs can be systematically adjusted by the judicious choice of metal-containing secondary building units and/or bridging organic linkers.<sup>2</sup>

This superior feature is very important to develop novel microporous materials for their selective sorption behaviors and thus for gas separation in which smaller molecules can go through the microporous channels while larger substrates

are blocked.<sup>3–16</sup> On the basis of the well-established approach to constructing  $\alpha$ - $P_0$  types of microporous 3D primitive cubic MOFs  $M(R(COO)_2)(L)_{0.5} \cdot xG$  [ $M^{2+} = Cu^{2+}$  and  $Zn^{2+}$ ;  $R(COO)_2 =$  dicarboxylate linker;  $L =$  bidentate pillar linker;  $G =$  guest molecules],<sup>17–28</sup> we have successfully utilized such a simple strategy to systematically tune the micropores by

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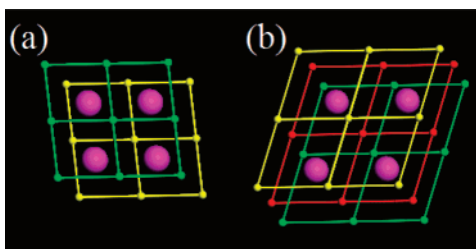
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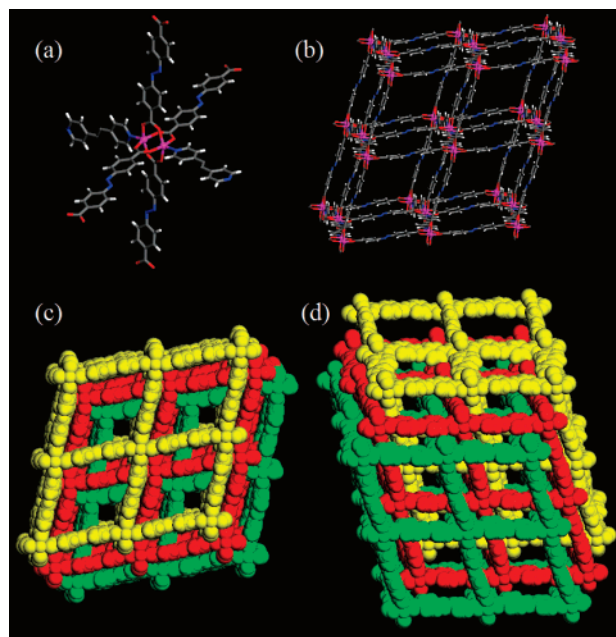
**Figure 1.** Double- and triple-framework interpenetration to tune micropores within MOFs.

double-framework interpenetration (Figure 1a) and explore their functional properties for the separation of small gas molecules, alkanes, and hexane isomers.<sup>29–32</sup>

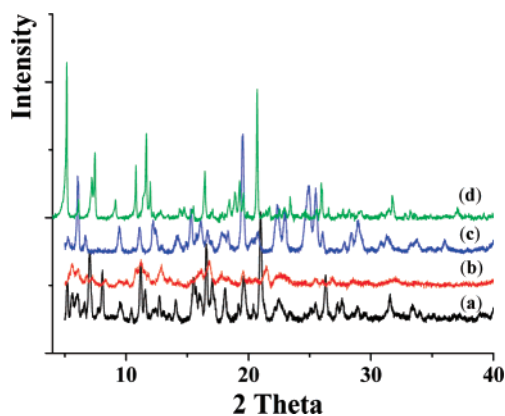
It is expected that the introduction of longer dicarboxylates and bidentate pillar linkers will lead to the formation of multiply interpenetrated frameworks, which have largely been overlooked for their recognition of small molecules.<sup>33,34</sup> To the best of our knowledge, very few multiply interpenetrated MOFs have been realized to exhibit permanent porosity.<sup>25,34</sup> Herein we report a rare example of a triply interpenetrated cubic net (Figure 1b), Zn(ADC)(4,4'-Bpe)<sub>0.5</sub>·2.5DMF·0.5H<sub>2</sub>O [**1**; ADC = 4,4'-azobenedicarboxylate, 4,4'-Bpe = *trans*-bis(4-pyridyl)ethylene, DMF = *N,N*-dimethylformamide], with pores of about 3.4 × 3.4 Å, for highly selective separation of H<sub>2</sub>/N<sub>2</sub>, H<sub>2</sub>/CO, and CO<sub>2</sub>/CH<sub>4</sub>.

**1** was synthesized by the solvothermal reaction of H<sub>2</sub>ADC, 4,4'-Bpe, and Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O in DMF at 100 °C for 24 h as red block-shaped crystals. It was formulated as Zn(ADC)-(4,4'-Bpe)<sub>0.5</sub>·2.5DMF·0.5H<sub>2</sub>O by elemental microanalysis and single-crystal X-ray diffraction studies, and the phase purity of the bulk material was independently confirmed by powder X-ray diffraction (PXRD) and thermogravimetric analysis (TGA).<sup>35,36</sup>

As expected, the framework is composed of paddle-wheel dinuclear Zn<sub>2</sub> units that are bridged by ADC dianions and further pillared by 4,4'-Bpe to form a 3D triply interpen-



**Figure 2.** X-ray crystal structure of MOF **1** showing (a) a paddle-wheel building unit and the coordination geometries, (b) one of the three independent primitive cubic nets, (c) a 1D channel of 3.4 × 3.4 Å along the *c* axis, and (d) a 1D channel of 3.6 × 3.6 Å viewed along the rectangular diagonal of the paddle-wheel clusters (zinc, pink; carbon, gray; nitrogen, blue; oxygen, red; hydrogen, white).

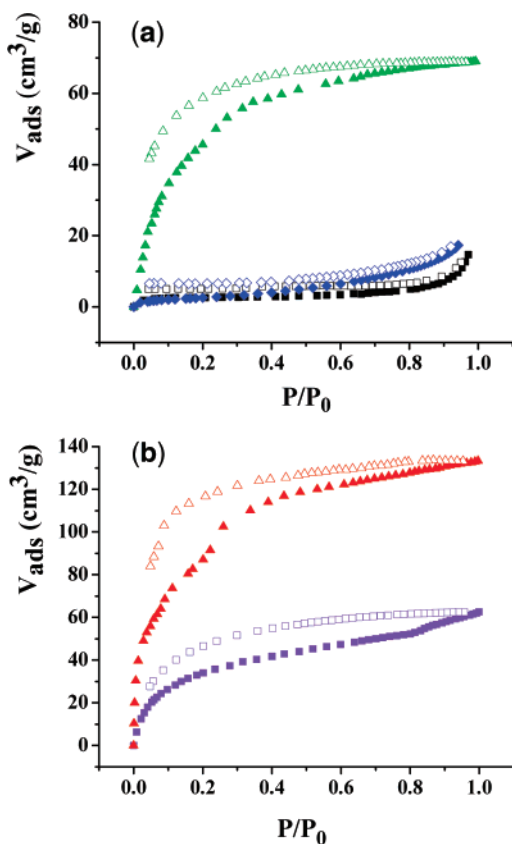


**Figure 3.** XPRD patterns of the as-synthesized **1** (black), methanol-exchanged **1** (red), activated **1a** (blue), and DMF-regenerated **1'** (green).

etrated elongated primitive cubic ( $\alpha$ -*P*<sub>0</sub>) structure. Because of the triple interpenetration of the 3D frameworks, the pores of MOF **1** are reduced to ca. 3.4 × 3.4 Å along the *c* axis (Figure 2c) and ca. 3.6 × 3.6 Å along the rectangular diagonal of the paddle-wheel clusters (Figure 2d).

**1** exhibited less framework transformations and/or deformations compared to those doubly interpenetrated MOFs Zn-(BDC)(4,4'-Bipy)<sub>0.5</sub> and Zn(NDC)(4,4'-Bpe)<sub>0.5</sub>,<sup>29,30</sup> partly because the three independent nets within **1** are enforced by van der Waals interactions. Immersing the as-synthesized **1** (Figure 3a) in pure methanol broadened the XPRD pattern (Figure 3b), while activation of the methanol-exchanged **1** at 150 °C under vacuum overnight led to the formation of an activated **1a** that has high crystalline form (Figure 3c). Immersing **1a** into pure DMF generated **1'** (Figure 3d), whose XPRD is slightly different from that of **1**. Such different XPRD patterns are attributed to the framework dynamics

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- (35) Synthesis of **1**: A mixture of Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.279 g, 0.936 mmol), H<sub>2</sub>ADC (0.253 g, 0.936 mmol), and 4,4'-Bpe (0.085 g, 0.466 mmol) was suspended in DMF (100 mL) and heated in a vial (400 mL) at 100 °C for 24 h. The red block-shaped crystals formed were collected, washed with DMF and hexane, and dried in air (0.50 g, 85%). Elem anal. Calcd for Zn(ADC)(4,4'-Bpe)<sub>0.5</sub>·2.5DMF·0.5H<sub>2</sub>O (C<sub>27.5</sub>H<sub>31.5</sub>N<sub>5.5</sub>O<sub>7</sub>Zn): C, 52.07; H, 5.01; N, 12.14. Found: C, 52.04; H, 5.06; N, 12.32.
- (36) Crystal data for **1**: C<sub>66</sub>H<sub>54</sub>N<sub>11</sub>O<sub>14</sub>Zn<sub>3</sub>, monoclinic, space group C2/c, *a* = 20.1473(13) Å, *b* = 27.5052(18) Å, *c* = 32.588(2) Å,  $\beta$  = 97.021(3)°, *V* = 17924(2) Å<sup>3</sup>, *Z* = 8, *D*<sub>calc</sub> = 1.053 g cm<sup>-3</sup>,  $\mu$  = 0.850 mm<sup>-1</sup>, *T* = 173 K, *F*(000) = 5832, 51 679 reflections collected, 12 632 independent reflections (*R*<sub>int</sub> = 0.0722), which were used in all of the calculations. Final residuals (for 847 parameters) were *R*<sub>1</sub> [*I* > 2σ(*I*)] = 0.0477 and *wR*<sub>2</sub> (all data) = 0.1564. CCDC 649367.



**Figure 4.** Gas-sorption isotherms of **1a** (a) at 77 K (hydrogen, green; nitrogen, blue; carbon monoxide, black) and (b) at 195 K (carbon dioxide, red; methane, violet; solid and open shapes represent adsorption and desorption, respectively).

and robustness of **1**, a very typical feature of the interpenetrated frameworks in which subtle differences of guest content and composition will lead to slightly different structures and thus PXRD patterns.<sup>2b,22,29–32</sup>

TGA studies indicate that **1** lost two types of solvent in the temperature range of room temperature to 180 °C and the activated **1a** is thermally stable up to about 300 °C. To examine the permanent porosity and thus to establish the feasibility of **1** for selective gas sorption, **1a** was examined for its gas-sorption properties. Sorption studies show that **1a** can take up a moderate amount of hydrogen at 1 atm and 77 K [69.0 cm<sup>3</sup> g<sup>-1</sup> (STP) or 0.62 wt %], exhibiting highly

selective sorption of hydrogen (kinetic diameter: 2.8 Å) over nitrogen (3.64 Å) and carbon monoxide (3.76 Å) (Figure 4a).<sup>37</sup> **1a** also exhibits selective sorption of carbon dioxide (3.3 Å) over methane (3.8 Å) at 195 K (Figure 4b). The Brunauer–Emmett–Teller surface area of **1a** is calculated to be about 100 m<sup>2</sup> g<sup>-1</sup> based on the carbon dioxide adsorption isotherm. The hydrogen storage capacity of **1a** is quite high for such a low surface area material, as rationalized by Thomas on a variety of microporous materials.<sup>38</sup> Because of the dynamic nature of such an interpenetrated framework, the sorption isotherms show typical hysteretic behaviors with respect to hydrogen, carbon dioxide, and methane.<sup>2b</sup>

In conclusion, a rare example of a triply interpenetrated MOF was rationally designed and structurally characterized, exhibiting highly selective sorption of gas molecules. The rational design approach to construct pillared paddle-wheel cubic ( $\alpha$ - $P_0$ ) nets, together with the richness of dicarboxylates and bidentate organic linkers of variable length and space, has made such a strategy especially interesting to tune the micropores of MOFs for their recognition and separation of small molecules by taking advantage of framework interpenetration. We are currently exploring a variety of microporous MOFs of  $\alpha$ - $P_0$  nets for their potential applications in gas storage and separation.

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**Supporting Information Available:** X-ray data in CIF format, experimental synthesis, crystal structure of **1**, PXRD pattern, and TGA. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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