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Robust Metal−Organic Framework Enforced by Triple-Framework Interpenetration Exhibiting High H₂ Storage Density

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A microporous metal−organic framework **1** $Zn_2(CNC)_2(DPT) \cdot G$ [CNC = 4-Carboxycinnamic; DPT = 3,6-Di-4-pyridyl-1,2,4,5-tetrazine; G = guest molecules] was synthesized and structurally characterized by a triply interpenetrated primitive cubic net with 1D pores of about 3.7 Å. **1** is highly robust enforced by triple framework interpenetration through weak van der Waals interactions, thus the activated **1b** takes up 1.28 wt % hydrogen gas and exhibits high hydrogen storage density of 95.2% at 1 atm and 77 K.

Introduction

Realization of permanent porosity is the prerequisite of porous MOFs for their application in gas storage, separation, and heterogeneous catalysis.[1–35] Although numerous amounts of MOFs have been structurally characterized, there are still few percent of MOFs with permanent porosity. It is generally believed that rigid metal-containing secondary building

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blocks such as a binuclear paddle-wheel $M_2(COO)_6$ (M = Cu^{2+} and Zn^{2+}) and tetranuclear $Zn_4O(COO)_6$, and rigid organic linkers such as BDC,[3] BTC,[4] and BPTC[5] favor the construction of robust MOFs with high porosity. As nature abhors a vacuum, there exists dilemma in the construction of robust porous MOFs in which frameworks tend to be interpenetrated and/or interwoven to fill the void space, and most structurally porous MOFs collapse to form nonporous MOFs once the guest solvent molecules are removed under vacuum. It needs to be noted that some flexible secondary building blocks and organic linkers have been also incorporated into the construction of porous MOFs, sometimes leading to the formation of a unique type of dynamic porous MOFs, which exhibit very interesting temperature- and/or pressure-dependent adsorption behaviors with respect to different guest molecules.[6–14]

To construct permanent pores, the frameworks need to be stabilized, which can be fulfilled by framework interpenetration through some collaborative weak $\pi\cdots\pi$ and C−H$\cdots$phenyl interactions. In fact, we have exemplified one highly robust interwoven MOF-14 $Cu_3(BTB)_2(H_2O)_3$ enforced by such weak framework interactions.[15] Recently Lin,[16] Zhou[17] and Long[18] have made use of framework interpenetration to enhance hydrogen storage capacities of MOFs. During our systematic studies on paddle-wheel based α-P_0 type microporous cubic MOFs $M[R(COO)_2](L)_{0.5}\cdot G$ (M^{2+} = Cu^{2+}, Zn^{2+} and Co^{2+}; $R(COO)_2$ = dicarboxylate linker; L = bidentate pillar linker; G = guest molecules) for their gas storage and separation, we have realized that shorter organic linkers favor the formation of robust doubly interpenetrated MOFs, whereas longer organic linkers tend to form dynamic doubly interpenetrated MOFs.[8–10] However, when organic linkers are very long, the structurally highly porous interpenetrated MOFs might be transformed into nonporous MOFs once they are activated under vacuum and such framework transformation is not reversible. Herein, we report a rare example of robust α-P_0 type cubic MOF **1** $Zn_2(CNC)_2(DPT)\cdot(DMF)_{1.5}(H_2O)$ (CNC = 4-carboxycinnamate; DPT = 3,6-Di-4-pyridyl-1,2,4,5-tetrazine;[36] DMF

= N,N-dimethylformamide), which is enforced by triple framework interpenetration, exhibiting high H_2 storage density.

Experimental Section

Materials and Method. All reagents and solvents employed were commercially available and used as supplied without further purification. TGA data were obtained on a TGA G500 V5.3 Build 171 instrument with a heating rate of 5 °C/min under an 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.

Synthesis of MOF 1. A mixture of $Zn(NO_3)_2\cdot6H_2O$ (0.279 g, 1 mmol), H_2CNC (0.2 g, 1 mmol), and DPT (0.12 g, 0.5 mmol) was suspended in DMF (100 mL) and heated in a vial (400 mL) at 80 °C for 24 h. The red block-shaped crystals formed were collected, washed with DMF, and dried in air (Yield: 60%, based on H_2CNC). Elem Anal. Calcd for $Zn_2(CNC)_2(DPT)\cdot(DMF)_{1.5}$-$(H_2O)$ $(C_{36.5}H_{32.5}N_{7.5}O_{10.5}Zn_2)$: C, 50.25; H, 3.76; N, 12.05. Found: C, 50.31; H, 3.3; N, 12.18. A sample of MOF **1** was soaked in methanol, filtered, and activated under high vacuum at 75 and 120 °C overnight to get MOF **1a** or **1b**, respectively.

Single-Crystal X-ray Crystallography. Diffraction intensities for **1** were collected on a computer-controlled Bruker SMART CCD diffractometer equipped with graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation at room temperature using the ω-scan technique. Raw data for all structures were processed using *SAINT*, and absorption corrections were applied using *SADABS*. Intensity data for **1a** 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. 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-678555 (**1**) contains the supplementary crystallographic data for this article. The data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB21EZ, U.K.; fax: (44) 1223−336−003; e-mail: deposit@ccdc.cam.ac.uk).

Gas Sorption Measurements. A Beckman Coulter SA3100 surface area analyzer was used to measure gas adsorption. To remove guest solvent molecules in the framework, the fresh sample soaked in methanol was filtered and vacuumed at 75 or 120 °C

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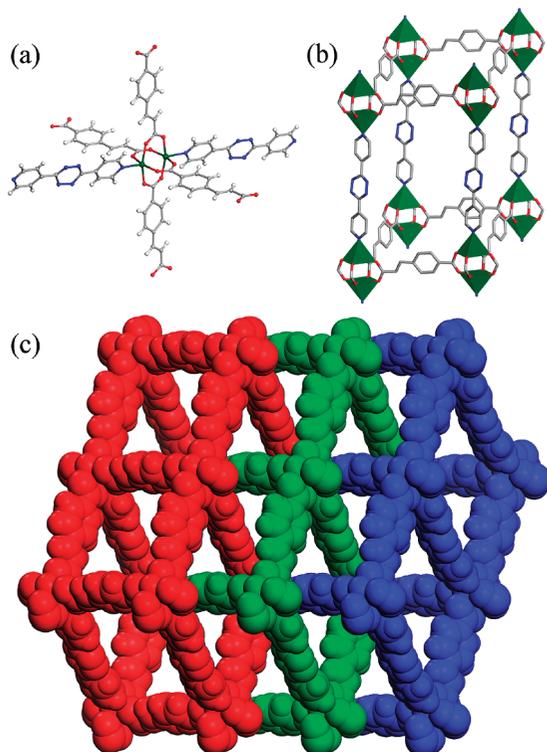
Figure 1. X-ray crystal structure of **1** showing (a) the coordination geometry of the paddle-wheel Zn₂(CNC)₂(DPT) building unit, (b) one of the three independent primitive cubic nets (zinc, green; carbon, gray; nitrogen, blue; oxygen, red; hydrogen, white); (c) a 1D triangular channel of 3.7 Å viewed along the rectangular diagonal of the cubic lattice.

overnight. Before the measurement, the sample was vacuumed again using the outgas function of the surface area analyzer for 2 h at 75 or 120 °C. A sample of 90.0 mg was used for the sorption measurement and was maintained at 77 K with liquid nitrogen, 87 K with liquid argon, and 195 K with an acetone/dry ice slush, respectively.

Results and Discussion

1 was synthesized by the solvothermal reaction of H_2CNC, DPT, and Zn $(NO_3)_2 \cdot 6H_2O$ in DMF at 80 °C for 24 h as red block-shaped crystals. It was formulated as $Zn_2(CNC)_2$-$(DPT) \cdot (DMF)_{1.5}(H_2O)$ 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) (part a of Figure 2) and thermogravimetric analysis (TGA) (Figure S5 in the Supporting Information).

As expected, the framework of **1** is composed of paddle-wheel dinuclear $\{Zn_2(COO)_4\}$ units (part a of Figure 1), which are bridged by CNC ligands to form a distorted 2D square grid. The 2D square grids are pillared by DPT molecules, whose nitrogen atoms occupy the axial sites of the $\{Zn_2(COO)_4\}$ paddle wheels, to form a 3D framework with a topology that can be described as an elongated primitive cubic (α-P_0) net (part b of Figure 1). The long DPT linker favors the construction of triply interpenetrated MOF, in which there exists only 1D triangular channels along the *a* axis of about 3.7 Å in diameter (part c of Figure 1), taken into the van der Waals radius. The effective free volume of **1** is calculated by *PLATON* analysis as being
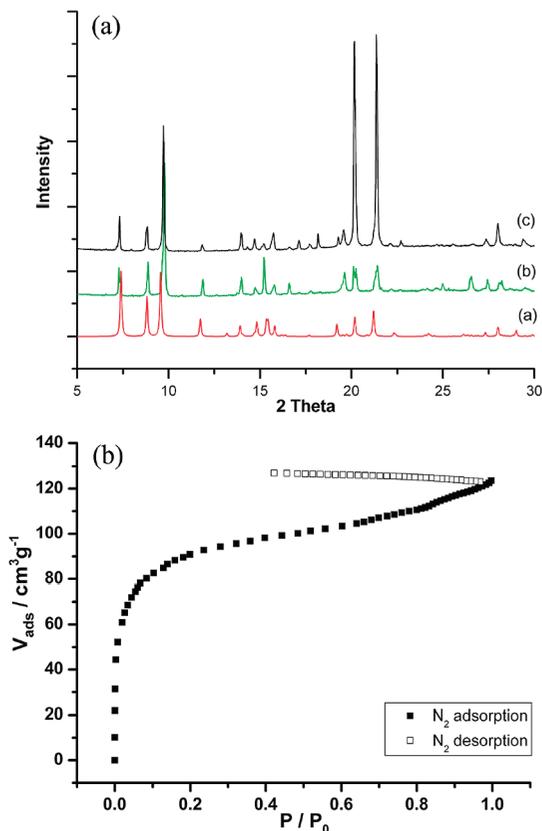
Figure 2. (a) PXRD patterns of the simulated PXRD pattern calculated from the single-crystal structure of **1** (a, red), methanol-exchanged (b, green) and the activated guest-free sample **1b** (c, black); and (b) N₂ adsorption isotherm of **1b** at 77 K (solid and open shapes represent adsorption and desorption, respectively).

27.4%. Unlike those dynamic MOFs, **1** is robust, which is enforced by triple framework interpenetration through van der Waals interactions, as confirmed by both PXRD and single-crystal X-ray diffraction studies (part a of Figure 2).

The methanol-exchanged **1** was gradually activated for their gas storage and separation functions. When it was activated at 75 °C under high vacuum overnight, the activated phase **1a** can take up quite a large amount of hydrogen (117 cm³/g) but a negligible amount of nitrogen (part a of Figure 3), underlying the capacity of **1a** for H_2/N_2 separation. **1a** was further activated at a higher temperature of 120 °C under high vacuum overnight to form **1b** in which all the guest solvent molecules were completely removed. The nitrogen sorption isotherm of **1b** (part b of Figure 2) shows typical type I sorption behavior with a Langmuir surface area (A_s) of 342 m²/g and a pore volume of 0.19 cm³/g, which is significantly higher than the triple-interpenetrated dynamic analogy $Zn(ADC)(4,4'-Bpe)_{0.5}$ (100 m²/g).[10e] **1b** also exhibits selective sorption of CO_2 (3.3 Å) over CH_4 (3.8 Å) at 195 K (part b of Figure 3).[37] Of the most interesting is the high hydrogen uptake of 1.28 wt % [142.6 cm³ g⁻¹ (STP)] at 1 atm for such low porous MOFs (part a of Figure 4), as rationalized by Thomas, Zhou, and others on a variety of microporous materials.[2]

It needs to be noted that the density for adsorbed H_2 of **1b** is 0.0674 g/cm³ is based on the measured pore volume

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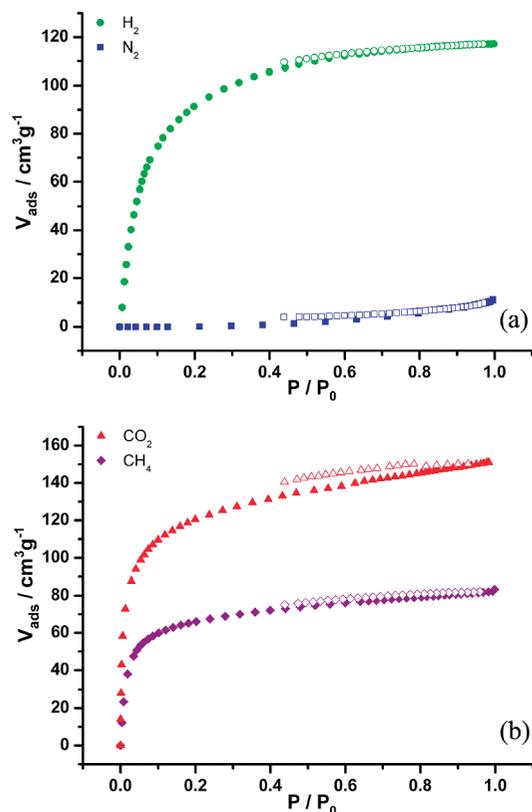
Figure 3. Gas adsorption isotherms of (a) **1a** at 77 K (hydrogen, green/circle; nitrogen, blue/square); and (b) **1b** at 195 K (carbon dioxide, red/triangle; methane, purple/rhombus; solid and open shapes represent adsorption and desorption, respectively).

(0.19 cm³/g), thus the fraction of the pore volume filled by liquid H_2 ($\rho H_2 = 0.0708$ g/cm³)[38] is 95.2% at 1 atm and 77 K, suggesting that H_2 is saturated and highly compressed within the pores of **1b** even at 1 atm.

To determine the hydrogen affinity of **1b**, an H_2 adsorption isotherm at 87 K was also collected to calculate the heat of adsorption, and the data were fit using the Langmuir−Freundlich equation.[39] Isosteric adsorption enthalpies as a function of the quantity of hydrogen adsorbed were calculated using a variant of the Clausius−Clapeyron equation (part b of Figure 4).[22] At low coverage, **1b** exhibits a moderate high H_2 adsorption enthalpy of 7.85 kJ/mol, which is higher than that of MOF-5 (5.2 kJ/mol), HKUST-1 (6.6 kJ/mol), or Prussian blue (7.4 kJ/mol) but is lower than that of MOF-74 (8.3 kJ/mol), IRMOF-11 (9.1 kJ/mol), a magnesium MOF (9.5 kJ/mol), or PCN-9 (10.1 kJ/mol).[22–24]

Multiply interpenetrated robust MOFs are very rare.[40] We have successfully constructed a robust triply interpenetrated microporous MOF, exhibiting high H_2 storage density. Small

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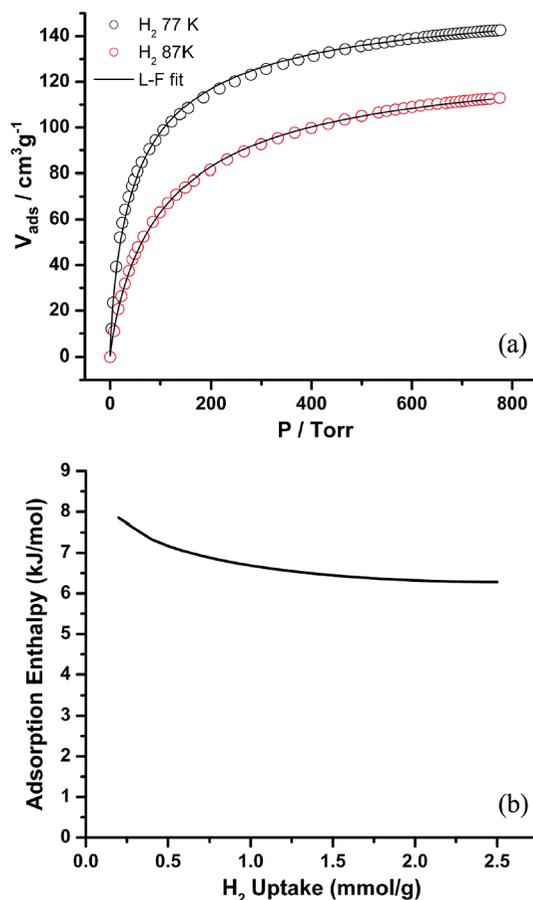
Figure 4. (a) H_2 adsorption isotherms of **1b** at 77K (black circles) and 87K (red circles). Solid lines correspond to Langmuir−Freundlich fits to the experimental data; (b) Hydrogen adsorption enthalpy for **1b** calculated from the hydrogen adsorption isotherms at 77 and 87 K.

pores within MOFs might enhance their interactions with hydrogen molecules and exhibit high H_2 storage density at low temperature and pressure, but such hydrogen storage capacity is limited by both the small pore space and the moderate hydrogen adsorption enthalpy, thus immobilization of chemisorptions' sites within porous MOFs will be certainly necessary to explore high hydrogen uptake MOFs at moderate temperature and pressure.

Supporting Information Available: Crystallographic data, extensive figures, and thermogravimetric analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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