DOI: 10.1021/cg100316s

A New Multidentate Hexacarboxylic Acid for the Construction of Porous Metal–Organic Frameworks of Diverse Structures and Porosities

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Received March 10, 2010; Revised Manuscript Received April 15, 2010

ABSTRACT: Three porous metal–organic frameworks have been constructed from the new developed C3-symmetric hexacarboxylic acid 3,3',3'',5,5',5''-benzene-1,3,5-triyl-hexabenzoic acid (H₆BHB) of different NaCl- and Al₂O₃-type topologies. The activated metal–organic frameworks (MOFs) exhibit permanent porosities as revealed in their gas and vapor adsorption isotherms, highlighting the promise of this new ligand for the construction of porous MOFs for gas storage and separation.

Introduction

The development of new multidentate carboxylic acids has played a very important role in the pursuit of novel porous metal-organic frameworks (MOFs) with interesting structures and practically useful functionalities and applications in gas storage.¹⁻³² Among the diverse explored carboxylic acids, those consisting of *m*-benzenedicarboxylic acid unit are of particular interest and importance because of the uniqueness of the *m*-benzenedicarboxylate unit to construct and stabilize porous MOFs of optimized pore structures and permanent open metal sites for gas storage.^{17–30} In fact, the prototypical MOF of such series of porous materials, Cu₃(BTC)₂(H₂O)₃ (HKUST-1),¹⁷ has been widely utilized as the storage media for hydrogen, methane, carbon dioxide, and acetylene, while the discovery of 3,3',5,5'-biphenyltetracarboxylic acid (H₄BPTC) for the construction of highly porous and robust MOF-505 has initiated the realization of a series of MOF-505 analogies for their extraordinarily high hydrogen, methane, and acetylene storage capacities simply by the implementation of different organic backbones to tune the pore structures and the porosities.^{18–27} Motivated by the power of 4,4',4''-benzene-1,3,5-triyl-tribenzoic acid (H₃BTB) for the assembly of highly porous MOFs as exemplified in MOF-14³¹ and MOF-177, 32 we have recently incorporated the *m*-benzenedicarboxylate unit and thus developed a new multidentate carboxylic acid 3,3',3",5,5',5"-benzene-1,3,5-triyl-hexabenzoic acid (H₆BHB) for the construction of porous MOFs. Herein we report the synthesis of this new multidentate hexacarboxylic acid and the construction of three porous MOFs with diverse structures and porosities.

Experimental Section

Chemicals. The chemicals with reagent-grade quality were purchased from commercial sources and used without purification.

Measurements. Thermogravimetric analyses (TGA) were performed on a Mettler Toledo TGA/SDTA851 analyzer in air with a heating rate of 5 K \cdot min⁻¹, from 30 to 800 °C. X-ray powder diffraction (XRD) patterns were measured using a Bruker D4 powder diffractometer at 40 kV, 40 mA for Cu K α radiation ($\lambda = 1.5418$ Å), with a scan speed of 0.2 s/step and a step size of 0.02° (2 θ). The elemental analyses were performed using Perkin-Elmer 240 CHN analyzers. The gas sorption isotherms were measured using a Micromeritics ASAP 2020 volumetric gas adsorption instrument. A freshly prepared sample of MOF-1 (167 mg) was soaked in CH₂Cl₂ to remove DMF guest molecules, loaded, and then activated by heating to 50 °C for 16 h until the outgas rate was < 5 μ mHg/min prior to the measurements. The sorption isotherms for methanol were recorded with an automatic gravimetric adsorption apparatus (IGA-003 series, Hiden Isochema Ltd.) at 298 K. The freshly prepared sample of MOF-3 (45 mg) was activated at 373 K under high vacuum for 12 h prior to measurements.

Single Crystal X-ray Structure Determination. Single crystal X-ray data of MOFs were collected using the microcrystal diffraction beamline 15ID-B at the Advanced Photon source in Argonne National Laboratory. Data were collected on Bruker D8 Diffractrometer equipped with APEX II detector. Data integration and reduction were using APEX suite software. The structure was solved by direct methods and subsequent difference Fourier syntheses and refined using the SHELXTL software package.^{33,34} The H atoms on the ligand were placed in idealized positions and refined using a riding model. The H atoms of the coordinated H₂O molecules could not be located, but were included in the formula. The unit cell includes a large region of disordered solvent molecules, which could not be modeled as discrete atomic sites. We employed PLATON/SQUEEZE to calculate the diffraction contribution of the solvent molecules and thereby producing a set of solvent-free diffraction intensities.³⁵ The detailed crystallographic data are shown in Table 1.

Synthesis of H₆BHB. H₆BHB was synthesized via Suzuki coupling of diethylisophthalate-5-boronic acid and 1,3,5-tribromobenzene as shown in Scheme 1. Ten grams of 5-amino-isophthalic acid dimethyl ester (1) was dissolved in 225 mL of 15% hydrobromic acid and cooled to 5 °C. Twenty-three milliliters of 2.5 M sodium nitrite solution was introduced slowly by rapid stirring, giving a solution of diazonium bromide. The solution of diazonium bromide was added to a solution containing 9.8 g of CuBr and 90 mL of 15% of hydrobromic acid under stirring, and the temperature was kept under 5 °C. After the addition was completed, it was kept stirring under room temperature for 2 h. The organic layer was separated and washed three times with water, dried with MgSO₄, filtered, and concentrated in a vacuum. The crude product was purified by column chromatography to obtain dimethyl 5-bromo-benzene-1,3-dicarboxy-late (2) as a brown powder. Yield 86%. ¹H-NMR (400 MHz, CDCl3): $\delta = 3.95$ (s, 6 H), 8.35 (d, 2 H), 8.61 (s, 1H) ppm.

Benzene-1,3,5-tris(3',5'-benzenedicarboxylic acid dimethyl ester) (3) was synthesized by stirring the mixture of 2 (2.7 g, 9.9 mmol),



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MOF	1	2	3
formula	C30 H12 O13 Zn4	C40.5 H39 N3 O16.5 Zn3	C33 H26 Cd3 N O17
formula weight	841.88	1026.35	1045.75
<i>T</i> (K)	90(2)	90(2)	90(2)
crystal system, space group	trigonal, R3c	trigonal, R3c	monoclinic, $C2/c$
$a(\dot{A})$	15.1785(7)	22.6021(3)	32.476(11) Å
$b(\dot{A})$	15.1785(7)	22.6021(3)	23.135(8)
$c(\dot{A})$	39.085(3)	39.7213(4)	18.163(6)
a (deg)	90	90	90
β (deg)	90	90	112.301(6)
γ (deg)	120	120	90
$V(Å^3)$	7798.2(7)	17573.2(4)	12626(7)
Z	6	12	8
$\rho_{\rm calc} ({\rm Mg/m^3})$	1.076	1.164	1.100
$\mu (\text{mm}^{-1})$	1.863	1.274	1.046
F(000)	2496	6282	4088
crystal size (mm)	$0.06 \times 0.06 \times 0.05$	$0.15 \times 0.15 \times 0.12$	$0.20 \times 0.10 \times 0.10$
θ range (°)	1.87-24.99	1.46-27.00	1.11-19.64
limiting indices	$-17 \le h \le 18, -18 \le k \le 18, \\ -45 \le l \le 46$	$\begin{array}{l} -28 \leq h \leq 28, -28 \leq k \leq 28, \\ -50 \leq l \leq 50 \end{array}$	$\begin{array}{l} -25 \leq h \leq 30, -21 \leq k \leq 21, \\ -17 \leq l \leq 17 \end{array}$
reflections collected/	14713/3054	49080/8544	16448/5582
unique	[R(int) = 0.0895]	[R(int) = 0.0654]	[R(int) = 0.1478]
completeness	99.9% (theta = 24.99)	100.0% (theta = 27.00)	99.8% (theta = 19.64)
data/restraints/parameters	3054/51/132	8544/1/380	5582/48/487
goodness-of-fit on F^2	1.158	1.067	0.906
final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.1160, wR_2 = 0.3012$	$R_1 = 0.0454, wR_2 = 0.1161$	$R_1 = 0.0622, wR_2 = 0.1420$
<i>R</i> indices (all data)	$R_1 = 0.1406, wR_2 = 0.3203$	$R_1 = 0.0517, wR_2 = 0.1187$	$R_1 = 0.0973, wR_2 = 0.1505$
largest diff peak and hole (e $Å^{-3}$)	1.053 and -0.945	0.886 and -0.375	0.935 and -0.947





^{*a*}(a) NaNO₂, 15% HBr, CuBr; (b) PdCl₂(dppf), KOAc, 1,4-dioxane; (c) Pd(PPh₃)₄, K₃PO₄, 1,4-dioxane, TMB; (d) 10 M aq NaOH, MeOH, H₂O, reflux overnight.

bis(pinacolato)diborane (3.0 g, 11.8 mmol), potassium acetate (2.8 g, 28.6 mmol), Pd (dppf)₂Cl₂ (0.1 g, 0.14 mmol), and dried 1,4-dioxane (20 mL) at 100 °C overnight and afterward extracted with ethyl acetate (20 mL). The organic layer was dried with Na₂SO₃ and the solvent was removed in a vacuum. The crude product was purified by column chromatography (silica gel, ethylacetate/petroleum ether, 6 v%). Yield 69.3%. ¹H-NMR

(400 MHz, CDCl₃): δ = 1.26 (m, 12 H), 3.95 (s, 6 H), 8.63 (d, 2 H), 8.76 (s, 1H) ppm.

3 (16 g, 50 mmol), 1,3,5-tribromobenzene (TMB) (3.5 g, 11.1 mmol), and K₃PO₄ (21.2 g, 99.7 mmol) were mixed in 1,4-dioxane (150 mL), and the mixture was deaerated using N₂ for 10 min. Pd(PPh₃)₄ (0.3 g, 0.26 mmol) was added to the stirred reaction mixture and the mixture was heated at 90 °C for 48 h under N₂ after which 1,4-dioxane



Figure 1. The crystal structure of MOF-1 indicating (a) six BHB ligands connecting with the $Zn_4O(COO)_6$ SBU; (b) six $Zn_4O(COO)_6$ SBUs connecting with the BHB ligand; and (c) resulting NaCl-type framework topology.



Figure 2. (a) Ball-and-stick and (b) space-filling model viewing from the [010] direction in the crystal structure of MOF-1 indicating a one-dimensional pore of about 7.3×5.7 Å.



Figure 3. The crystal structure of MOF-2 indicating (a) four BHB ligands connecting with the dinuclear SBU; (b) six dinuclear SBUs connecting with the BHB ligand; (c) resulting cor topology.

was removed under a vacuum. The resultant solid was washed with water (30 mL) and methylene dichloride (60 mL), respectively, and then dried under a vacuum. The pure benzene-1,3,5-tris(3',5'-benzenedicarboxylic acid dimethyl ester) (**4**, 3.2 g) was filtered and dried after refluxing in MeOH for 24 h. Yield 43.8%. ¹H-NMR (400 MHz, CDCl₃): $\delta = 3.95$ (s, 18 H), 7.90 (d, 3 H), 8.55 (d, 6 H), 8.74 (s, 3H) ppm.

4 (3 g, 4.6 mmol) was then suspended in a mixture of THF (20 mL) and MeOH (20 mL), to which 50 mL of 10 M NaOH aqueous solution was added. The mixture was stirred under reflux overnight and the THF and MeOH were removed under a vacuum. Dilute HCl was added to the remaining aqueous solution until the solution was at pH = 3. The solid was collected by filtration, washed with water and MeOH, and dried to give H₆BHB (2.5 g,

95.8% yield). ¹H-NMR (400 MHz, DMSO): $\delta = 7.66$ (d, 3 H), 8.69 (d, 6 H), 8.96 (s, 3H) ppm.

Synthesis of MOF-1. A mixture of H_6BHB (5.4 mg, 0.010 mmol) and Zn(CH₃COO)₂·2H₂O (12.3 mg, 0.056 mmol) was dissolved in DMF (2 mL) in a screw-capped vial. After two drops of HNO₃ (63%, aq.) and 0.1 mL of H₂O were added to the mixture, the vial was capped and placed in an oven at 65 °C for 24 h. The resulting rhombic prism-shaped single crystals were washed with DMF several times to give MOF-1 (5.6 mg, yield: 60.1%). Elemental analysis: Calcd. for Zn₄O(BHB)·(DMF)(H₂O)₈ (C₃₃H₃₇NO₂₃Zn₄): C, 37.40; H, 3.30; N, 1.32; Found: C, 36.96; H, 2.80; N: 1.56.

Synthesis of MOF-2. A mixture of H_6BHB (6.7 mg, 0.011 mmol) and $Zn(NO_3)_2 \cdot 6H_2O$ (15.8 mg, 0.053 mmol) was dissolved in DMF (2 mL) and MeOH (1 mL) in a screw-capped vial. After two drops of

water were added to the mixture, the vial was capped and placed in an oven at 65 °C for 24 h. The resulting hexagonal prism-shaped single crystals were washed with DMF for several times to produce MOF-2 (7.4 mg, yield: 59.2%). Elemental analysis: Calcd. for Zn₃(BHB)(DMF)₃(MeOH)_{1.5} · (DMf) (C_{43.5}H₄₆N₄O_{17.5}Zn₃): C, 47.37; H, 4.17; N, 5.08; Found: C, 47.48; H, 4.60; N, 5.49.

Synthesis of MOF-3. A mixture of H_6BHB (5.0 mg, 0.009 mmol) and Cd(NO₃)₂·4H₂O (10.3 mg, 0.033 mmol) was dissolved in DMF (2 mL) and EtOH (1 mL) in a screw-capped vial. The vial was capped and placed in an oven at 65 °C for 24 h. The resulting polyhedral prism shaped single crystals were washed with DMF several times to produce MOF-3 (6.2 mg, yield: 57.2%).

Results and Discussion

Structure of MOF-1. A single-crystal X-ray crystallographic study reveals that 1 crystallizes in a noncentrosymetrical rhombohedral space group of R3c. It adopts a Zn₄O-(COO)₆ cluster as its secondary building units (SBUs). All the Zn centers in the cluster have tetrahedral geometry through coordination to a μ_4 -oxygen atom and three oxygen atoms of the bridging carboxylic groups. No coordinating solvent molecules are observed in the structure. Every Zn₄O- $(COO)_6$ cluster is surrounded by six BHB⁶⁻ units and each BHB^{6-} linker also connects six $Zn_4O(COO)_6$ clusters to form a three-dimensional (3-D) framework. The underlying topology of 1 is a 6-coordinated net with both the center of the octahedral $Zn_4O(COO)_6$ cluster and the center of the BHB⁶ unit as nodes (Figure 1a,b). Further topological analysis suggests that the framework of 1 can be described as NaCl-type topology (Figure 1c).^{36–39} The three isophthalate groups of each BHB^{6-} are noncoplanar as anticipated.



Figure 4. The crystal structure of MOF-**3** indicating (a) four BHB ligands connecting with the dinuclear SBU; (b) six dinuclear SBUs connecting with the BHB ligand; (c) resulting **cor** topology.

The adjacent phenyl rings are tilted relative to each other with dihedral angles of $31.1(3)^{\circ}$, generating elliptical-shaped pores with a size of 7.3×5.7 Å viewing from both [100] and [010] directions (Figure 2). The void volume in MOF-1 occupied by the guest solvent molecules is 57.6% calculated by the PLATON/VOID routine.³⁵

Structure of MOF-2. X-ray analysis reveals that 2 crystallizes in the noncentrosymetrical rhombohedral space group R3c. The asymmetric unit contains two zinc atoms, 3/2BHB⁶⁻, two coordinated DMF molecules and one coordinated methanol. Both zinc atoms are six-coordinated: one coordinate with six oxygen atoms from four carboxylic groups, while the other coordinates with three carboxylic oxygen atoms, two DMF and one methanol molecules. The two zinc atoms are connected by three bridging carboxylates into a noncentral symmetrical dinuclear SBU as a 4-connected node which is connected with four BHB ligands. On the other hand, each BHB ligand is connected with six dinuclear SBUs and considered as a 6-connected node. From the view of the topology, the 3-D frameworks shows distorted tetrahedral and octahedral coordination in a (4,6)connected structure, which is found to be the structure of the corundum form of Al₂O₃ (α -alumina with the symbol cor)³⁹ (Figure 3). The void volume of 2 is about 40.8% calculated by the PLATON/VOID routine. There is a small channel with a diameter of 3.5 Å along the [011] direction (Figure S1, Supporting Information).

Structure of MOF-3. MOF-3 crystallizes in the monoclinic space group of C2/c. The asymmetric unit contains three cadmium atoms, one BHB⁶⁻, one coordinated DMF, and four coordinated water molecules. The three cadmium atoms are 6-coordinated with a different coordination environment. Cd1 and Cd2 are connected by three carboxylates into a dinuclear SBU, while Cd3 are connected by the symmetryrelated Cd3A into another dinuclear SBU. Despite this difference, both dinuclear SBUs are linked by four ligands and can be considered as 4-connected nodes, featuring **3** also as a (4,6)-connected α -alumina **cor** structure (Figure 4). Different from MOF-**2**, MOF-**3** contains one type of straight open channel with a diameter of about 6.9 × 9.0 Å along the *c*-axis (Figure S2, Supporting Information). The void volume occupied by the guest solvent molecules is 55.3%.

Gas and Vapor Adsorption of MOF-1 and MOF-3. The structurally porous nature of MOF-1 and MOF-3 has encouraged us to examine their potential gas and vapor adsorption properties.



Figure 5. (a) Nitrogen and hydrogen isotherms at 77 K and (b) carbon dioxide and methane gas adsorption isotherms at 273 K for the activated 1.

Article



Figure 6. Methanol adsorption isotherm on the activated MOF-3 at 298 K.

The activated MOF-1 exhibits a typical type I N₂ adsorption isotherm with the Brunauer–Emmett–Teller (BET) and Langmuir surface areas of 156 and 209 m²/g, respectively (Figure 5). A plot of Horvath–Kawazoe (HK) differential pore volume indicates that 1 contains pores of ca. 5.2 Å opening which is in agreement with the X-ray structural analysis. The activated MOF-1 takes up 43.2 cm³/g hydrogen gas at 77 K and 1 atm (0.35 wt % H₂). Its carbon dioxide uptake (35.0 cm³/g) is about three times higher than its methane uptake (10.8 cm³/g) at 273 K, highlighting its potential application for the CO₂/CH₄ separation.

The activated MOF-3 does not take up any gas molecules; however, it does exhibit a type-I methanol adsorption isotherm with a methanol uptake of 6.5 wt % at 298 K and 160 mbar (Figure 6), indicating that the activated MOF-3 might be partially recovered back into the original porous structure of MOF-3.

In summary, we have successfully synthesized a new multidentate hexacarboxylic acid and incorporated it into three porous MOFs of different NaCl- and Al₂O₃-type topologies. The establishment of permanent porosities within these synthesized MOFs highlights the promise of this new organic linker for the construction of novel porous MOFs for gas storage and separation. Self-assembly of this organic linker with other metal ions/clusters is under progress in our laboratory to pursue some highly porous MOFs for gas storage and ultramicroporous MOFs for gas separation.

Acknowledgment. This work was supported by an Award CHE 0718281 from the NSF (BC). Z.C., Y.Z., and D.Z. thank the financial support from NSF of China. ChemMatCARS Sector 15 is principally supported by the National Science Foundation/Department of Energy under Grant No. NSF/CHE-0822838. Use of the Advanced Photon Source was supported by the U. S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357. We thank Dr. Shengqian Ma for his help for the collection of crystal diffraction data.

Supporting Information Available: X-ray crystallographic data in CIF format and XRD, TGA data for MOFs **1–3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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