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Supramolecular Isomerism of Metal–Organic Frameworks Derived from a Bicarboxylate Linker with Two Distinct Binding Motifs

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ABSTRACT: Two novel metal–organic frameworks (MOFs), $\text{Cu}(3,4'\text{-bpdcc})(\text{H}_2\text{O})\cdot\text{DMF}\cdot 2\text{H}_2\text{O}$ (**1**) and $\text{Cu}(3,4'\text{-bpdcc})(\text{H}_2\text{O})\cdot 2\text{DMF}\cdot 4.5\text{H}_2\text{O}$ (**2**), have been solvothermally synthesized by the reaction of an unsymmetrically substituted carboxylate ligand 3,4'-biphenyldicarboxylic acid (3,4'-bpdcc) and $\text{Cu}(\text{NO}_3)_2\cdot 2.5\text{H}_2\text{O}$. X-ray crystal structural analyses reveal that both MOFs possess the binuclear paddle-wheel units $[\text{Cu}_2(\text{O}_2\text{CR})_4]$, which are linked by the biphenyl connectors, to give two different three-dimensional (3-D) frameworks. The structural diversities are due to the different coordinated arrangements of the two distinct carboxylate groups. In **1**, the noncentral symmetrical A–A–B–B arrangement leads to an uncommon twisted Cu-paddlewheel unit, which favors a tetrahedral configuration to generate a 3-fold interpenetrating 3-D framework with a diamond topology. In **2**, the paddle-wheel unit constructed by the central symmetrical A–B–A–B arrangement of the ligand acts as a square-planar 4-connected node to give a 2-fold interpenetrating 3-D framework with an NbO topology. These two polymorphs are very rare in MOFs that exhibit similar metal local coordination geometry and the same secondary building units (SBU) but different ligands linking modes. Furthermore, both **1** and **2** possess large one-dimensional channels and show the ability to adsorb H_2 .

Introduction

Metal–organic frameworks (MOFs) have received great attention because of their amenability to design and extraordinary permanent porosity, which allow their applications in gas storage, catalysis, and separations.^{1–7} Over the past decades, a large number of highly symmetrical carboxylic acids represented by 1,4-benzenedicarboxylic acid (H_2bpc)^{8–10} and benzene-1,3,5-tricarboxylic acid (H_3btc)^{11–13} were widely adopted as organic linkers. To obtain MOFs with large pore sizes, symmetrical biphenyl acid derivatives with long linkers, such as biphenyl-4,4'-dicarboxylic acid (H_2bpdc), have been successfully used for the assembly of MOFs with nanoscale channels and cavities.^{14–16} Nowadays, more and more researchers are working on the unsymmetrically substituted carboxylate linkers, which are expected to form MOFs with novel geometries and properties.^{17–23} There are two kinds of unsymmetrically substituted carboxylate linkers according to the literature: (i) linkers with heteroatom or functional groups (except carboxyl groups) at the unsymmetrical positions of the highly symmetrical carboxylate ligands, (ii) linkers with identical carboxyl groups at the unsymmetrical positions. However, most MOFs constructed by the ligands from the first strategy are isostructural with their symmetrical parent compounds.^{17–22} Concerning the second kind of linkers, only one example has been reported in the literature.²³ This MOF, named UCM-150, was derived from the unsymmetrical ligands, biphenyl-3,4',5-tricarboxylic acid. A rare building unit of trinuclear Cu(II) cluster, $[\text{Cu}_3(\text{O}_2\text{CR})_6]$ as well as the ubiquitous Cu(II) paddle-wheel cluster, $[\text{Cu}_2(\text{O}_2\text{CR})_4]$, are formed by the distinct carboxylate groups on different positions. This sample offers entry into a variety of new linker types which still remain largely unexplored.

Herein, our strategy for preparing large porous frameworks is using a novel unsymmetrically substituted ligand 3,4'-bpdcc, which has two distinct carboxyl groups at 3- and 4'-position of

the biphenyl ring. We report in this article the synthesis and characterization of two MOFs, $\text{Cu}(3,4'\text{-bpdcc})(\text{H}_2\text{O})\cdot\text{DMF}\cdot 2\text{H}_2\text{O}$ (**1**) and $\text{Cu}(3,4'\text{-bpdcc})(\text{H}_2\text{O})\cdot 2\text{DMF}\cdot 4.5\text{H}_2\text{O}$ (**2**), from this ligand. Of particular interest, they are supramolecular isomers both constructed from the Cu(II) paddle-wheel units $[\text{Cu}_2(\text{O}_2\text{CR})_4]$ and the biphenyl linkers. Although the binuclear paddle-wheel unit has been reported as a common building block for metal-carboxylate frameworks construction, in those two structures, the two Cu(II) paddle-wheels are distinct due to the different coordination modes of the carboxylate groups from different positions. Such supramolecular isomers with network structural differences (termed “polymorphism”) are particularly rare for MOFs.^{24–26} Those two polymorphs **1** and **2** possess diamond and NbO net topologies, respectively. In spite of the structural interpenetrating, they exhibit large one-dimensional (1-D) channels and show the ability to adsorb H_2 .

Experimental Section

Materials and Methods. All reagents for syntheses were purchased from commercial sources and used as received. ^1H NMR spectra in solution were recorded on a JEOL ECA400 nuclear magnetic resonance spectrometer. Chemical shifts are given in ppm. Thermogravimetric analyses (TGA) were carried out with a Mettler Toledo TGA/SDTA851 analyzer in air with a heating rate of $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$. Elemental analyses were done on an Elementar Vario EL III microanalyzer. IR spectra were measured from a KBr pellets on a Nicolet Nexus 470 FT-IR spectrometer in the range $4000\text{--}400\text{ cm}^{-1}$. X-ray powder diffraction (XRD) patterns were measured using a Bruker D4 powder diffractometer at 40 kV, 40 mA with Cu K α radiation ($\lambda = 1.5418\text{ \AA}$), with a scan speed of 0.2 s/step and a step size of 0.02° (2θ). The sorption isotherms for hydrogen were measured with an automatic gravimetric adsorption apparatus (IGA-003 series, Hidden Isochema Ltd.) at 77 K. High purity hydrogen (99.999%) was used for the measurement. Before the measurements, the crystals of **1** and **2** was immersed in acetone for 48 h and then evacuated under a dynamic vacuum ($<10^{-3}$ Torr) at room temperature for 24 h to remove the guest solvates (DMF and H_2O). After the removal of acetone, the samples (weight 30–50 mg) were activated under 10^{-10} bar at 373 K for 16 h to give fully desolvated **1** and **2**.

Syntheses of 3,4'-bpdcc. 4-Carboxyphenylboronic acid (4.15 g, 25 mmol), 3-bromo-benzoic acid (5.03 g, 25 mmol), and K_2CO_3 (6.9 g,

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50 mmol) were dissolved in dimethyl ether (DME) (75 mL) and distilled water (75 mL). The mixture was degassed using N_2 . Then $Pd(PPh_3)_4$ (0.58 g, 0.5 mmol) was added, and the mixture was heated at 80 °C for 1 day under N_2 atmosphere. After cooling to room temperature, the liquor was collected by filtration and superfluous DME was removed. The solution was extracted three times with dichloromethane and acidified by concentrated hydrochloric acid. Pure dimethyl biphenyl-3,4'-dicarboxylate was obtained by passing through a SiO_2 column after etherifying the solid with methanol. The target product 3,4'-biphenyl-dicarboxylic acid was hydrolyzed by heating dimethyl biphenyl-3,4'-dicarboxylate in aqueous NaOH (1 M) under reflux, followed by acidification with aqueous HCl (37%), affording 3,4'-bpdc (4.53 g, yield: 74.8%). 1H NMR (400 MHz, $DMSO-d_6$): δ 13.09 (s, 2 H); 8.24 (s, 1 H); 8.06 (d, 2 H); 7.98 (d, 2 H); 7.86 (d, 2 H); 7.65 (t, 1 H). Elemental analysis calcd for 3,4'-bpdc ($C_{14}H_{10}O_4$): C 69.42, H 4.13; found: C 69.31, H 4.09.

Synthesis of $Cu(3,4'\text{-bpdc})(H_2O) \cdot DMF \cdot 2H_2O$ (1). Blue-green block crystals of **1** were obtained by the low-temperature solvothermal reaction. For a typical preparation, a mixture of 3,4'-bpdc (0.024 g, 0.1 mmol), $Cu(NO_3)_2 \cdot 2.5H_2O$ (0.024 g, 0.1 mmol), DMF (3 mL), C_2H_5OH (3 mL), and H_2O (3 mL) in a molar ratio of 1:1:388:515:1667 was heated at 60 °C for 48 h in a Teflon-lined stainless steel autoclave (15 mL). After cooling of the sample to room temperature, crystals of **1** were obtained with a yield of 80% based on 3,4'-bpdc. Elemental analysis calcd for **1** $C_{17}H_{21}NO_8Cu$ (430.90): C, 47.38; H, 4.91; N, 3.25%. Found: C, 46.68; H, 5.07; N, 3.22%. IR (cm^{-1}): 3416w, 2929m, 1659m, 1618m, 1563m, 1402s, 1100w, 762m, 694w.

Synthesis of $Cu(3,4'\text{-bpdc})(H_2O) \cdot 2DMF \cdot 4.5H_2O$ (2). A mixture of 3,4'-bpdc (0.024 g, 0.1 mmol), $Cu(NO_3)_2 \cdot 2.5H_2O$ (0.024 g, 0.1 mmol), DMF (7 mL), C_2H_5OH (1 mL), and H_2O (1 mL) in a molar ratio of 1:1:905:171.6:555 was heated at 60 °C for 48 h in a Teflon-lined stainless steel autoclave (15 mL). After cooling of the sample to room temperature, blue block crystals of **2** were obtained with the yield of 80% based on 3,4'-bpdc. Elemental analysis calcd for **2** $C_{20}H_{33}N_2O_{11.5}Cu$ (549.03): C, 43.75; H, 6.06; N, 5.10%. Found: C, 43.67; H, 6.09; N, 5.16%. IR (cm^{-1}): 3423w, 2929w, 1658m, 1621m, 1563m, 1400s, 1100w, 762m, 663w.

X-ray Crystallographic Study. Data of the two compounds were collected at room temperature using a Bruker APEX diffractometer equipped with a normal focus, 3.0 kW sealed tube X-ray source (Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å). Data reduction and cell refinement were performed with the SAINT program,²⁷ and the absorption correction program SADABS was employed to correct the data for absorption effects. The structures were solved by direct methods and refined using full-matrix least-squares treatment (SHELXTL-97)²⁸ with atomic coordinates and anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms on C atoms were positioned geometrically and the hydrogen atoms of water molecule were located in Fourier difference maps. Guest solvent molecules were highly disordered and were impossible to refine using conventional discrete-atom models. To resolve these issues, the contribution of solvent electron density was removed by the SQUEEZE routine in PLATON.^{29,30} CCDC-701722 (**1**) and -701723 (**2**) contain the supplementary crystallographic data for this paper. Copies of the data could be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB21EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk). The crystallographic data are summarized in Table 1; the selected bond lengths and angles are given in Table 2.

Results and Discussion

Synthesis. There are many synthetic parameters that influence the formation of MOFs, including metal source, metal-to-ligand ratio, solvent, concentration, pH, reaction temperature, and time. In the synthesis of **1** and **2**, the ratio of metal/pbdc, the types of solvents, reaction temperature, and time are all the same. It is interesting that the formation of **1** and **2** are adjustable by the ratio of the solvents. The mixed solvents of DMF, water, and alcohol are employed in the synthesis. Our experiments showed that the amounts of alcohol have no effect on the final products under the condition of the same DMF/ H_2O ratio. In the synthesis of **1**, we changed the amounts of alcohol with a ratio of DMF/ H_2O /alcohol from 1:1:5 to 1:1:0.2 and powder X-ray diffraction

Table 1. Crystal and Structure Refinement Data for Desolvated Compounds **1'** and **2'**

	1'	2'
formula	$C_{14}H_{10}CuO_5$	$C_{14}H_{10}CuO_5$
fw	321.76	321.76
space group	$I4(1)$	$R\bar{3}$
<i>a</i> (Å)	18.119(5)	31.681(15)
<i>b</i> (Å)	18.119(5)	31.681(15)
<i>c</i> (Å)	12.935(5)	14.297(10)
α (deg)	90	90
β (deg)	90	90
γ (deg)	90	120
<i>V</i> (Å ³)	4246(2)	12427(12)
<i>Z</i>	8	18
<i>D_c</i> (g cm ⁻³)	1.007	0.774
μ (mm ⁻¹)	1.038	0.798
<i>F</i> (000)	1304	2934
<i>T</i> (K)	298(2)	298(2)
reflns collected	7509	17456
reflns unique	3693	4877
<i>R</i> (int)	0.0870	0.0493
GOF on <i>F</i> ²	1.102	0.865
<i>R</i> ₁ , <i>wR</i> ₂ ^a [<i>I</i> > 2σ(<i>I</i>)]	0.0809, 0.2045	0.0362, 0.0830
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0885, 0.2087	0.0538, 0.0866
$\Delta\rho_{\max}/\Delta\rho_{\min}$ (e Å ⁻³)	0.552 and -1.026	0.288 and -0.230

$$^a R_1 = \sum |F_o| - |F_c| / \sum |F_o|, \quad ^b wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}.$$

(PXRD) patterns showed that the structures of final products are identical. The ratios of DMF/ H_2O /alcohol from 7:1:5 to 7:1:0.2 resulted in the same product of **2**. We could even obtain **1** and **2** without alcohol. The amounts of alcohol only affect the yield and morphology of the crystal products. So the ratio of DMF/ H_2O is the only factor which is responsible for the formation of the two polymorphs. When the voluminal ratio of DMF/ H_2O is 1:1, pure blue-green crystals of **1** can be obtained in a good yield. Blue crystals of **2** appear with the increase of DMF. The mixture of **1** and **2** is obtained during the ratio range of 1:1–7:1. When the ratio of DMF/ H_2O increases to 7:1, we can get pure crystals of **2**. Both powder X-ray diffraction (PXRD) patterns of products in the ratio of 1:1 and 7:1 are a good match with the simulated patterns from the single-crystal data of **1** and **2**, respectively, confirming the purity of the two compounds (Figure S1, Supporting Information).

Structural Descriptions. Single-crystal X-ray diffraction revealed that **1** crystallizes in a chiral space group $I4(1)$ and the asymmetric unit consists of one copper(II) ion, one 3,4-bpdc, and one coordinated water molecule. The Cu(II) is five coordinated in a square pyramidal geometry by four oxygen atoms from four different 3,4'-bpdc and a water molecule. Pairs of Cu(II) centers are bridged by four carboxylate groups from different 3,4'-bpdc ligands, forming a paddle-wheel secondary building unit (SBU) [$Cu_2(O_2CR)_4$]. Different from the common paddle-wheel SBU composed by four identical carboxyl groups,³¹ the paddlewheel SBU in **1** exhibits a distorted geometry due to the unequally carboxyl groups in different positions. The two carboxyl groups on the 3-position (labeled as A) and the other two on the 4'-position (labeled as B) of the 3,4'-bpdc ligands are coordinated with two Cu atoms along the Cu–Cu axis clockwise in an A–A–B–B arrangement (Figure 1a). The average Cu–O_c (O_c represent the carboxylate oxygens) distance is 1.979(7) Å, and Cu–O_w (O_w represent water molecule) has a longer distance of 2.138(8) Å, which is similar to those found in related [$Cu_2(O_2CR)_4$] paddle-wheel MOFs.³² However, both carboxylate groups on the 3- and 4'-positions are twisted from the corresponding linking phenyl rings with the dihedral angles 17.0° and 18.3° and the two phenyl rings also have to a certain extent a twist with a dihedral angle of 36.4°, which is larger than those observed in MOFs constructed

Table 2. Bond Lengths (Å) and Angles (°) for Desolvated Compounds 1 and 2

Compound 1 ^a			
Cu(1)–O(3)#1	1.928(7)	Cu(1)–O(4)#2	1.976(6)
Cu(1)–O(5)#3	2.005(6)	Cu(1)–O(2)	2.007(7)
Cu(1)–O(1)	2.138(8)	Cu(1)–Cu(1)#1	2.6347(19)
O(3)#1–Cu(1)–O(4)#2	170.5(3)	O(3)#1–Cu(1)–O(5)#3	87.7(3)
O(4)#2–Cu(1)–O(5)#3	89.4(3)	O(3)#1–Cu(1)–O(2)	89.2(3)
O(4)#2–Cu(1)–O(2)	90.7(3)	O(5)#3–Cu(1)–O(2)	161.9(3)
O(3)#1–Cu(1)–O(1)	96.1(4)	O(4)#2–Cu(1)–O(1)	93.3(4)
O(5)#3–Cu(1)–O(1)	100.7(4)	O(2)–Cu(1)–O(1)	97.4(4)
O(3)#1–Cu(1)–Cu(1)#1	86.0(2)	O(4)#2–Cu(1)–Cu(1)#1	84.59(18)
O(5)#3–Cu(1)–Cu(1)#1	81.80(18)	O(5)#3–Cu(1)–Cu(1)#1	81.80(18)
O(2)–Cu(1)–Cu(1)#1	80.19(18)	O(1)–Cu(1)–Cu(1)#1	176.7(3)
C(1)–O(3)–Cu(1)#1	122.6(6)	C(14)–O(4)–Cu(1)#4	119.9(6)
C(14)–O(5)–Cu(1)#5	122.3(5)		
Compound 2 ^b			
Cu(1)–O(5)#1	1.9495(17)	Cu(1)–O(2)	1.9584(18)
Cu(1)–O(3)#2	1.9652(18)	Cu(1)–O(4)#3	1.9665(17)
Cu(1)–O(1)	2.153(2)	Cu(1)–Cu(1)#2	2.6373(14)
O(5)#1–Cu(1)–O(2)	89.49(8)	C(14)–O(5)–Cu(1)#5	121.33(16)
O(2)–Cu(1)–O(3)#2	168.31(7)	O(5)#1–Cu(1)–O(3)#2	88.85(8)
O(2)–Cu(1)–O(4)#3	89.72(8)	O(5)#1–Cu(1)–O(4)#3	168.07(7)
O(5)#1–Cu(1)–O(1)	99.74(8)	O(3)#2–Cu(1)–O(4)#3	89.51(8)
O(3)#2–Cu(1)–O(1)	96.05(9)	O(2)–Cu(1)–O(1)	95.63(9)
O(5)#1–Cu(1)–Cu(1)#2	85.62(5)	O(4)#3–Cu(1)–O(1)	92.18(8)
O(3)#2–Cu(1)–Cu(1)#2	83.76(5)	O(2)–Cu(1)–Cu(1)#2	84.57(5)
O(1)–Cu(1)–Cu(1)#2	174.63(6)	C(1)–O(2)–Cu(1)	122.52(14)
C(1)–O(3)–Cu(1)#2	122.62(16)	C(14)–O(4)–Cu(1)#4	124.20(15)

^a Symmetry codes: #1 $-x + 2, -y + 1, z$; #2 $-y + 3/2, x, z + 3/4$; #3 $y + 1/2, -x + 1, z + 3/4$; #4 $y, -x + 3/2, z - 3/4$; #5 $-y + 1, x - 1/2, z - 3/4$. ^b Symmetry codes: #1 $-x + y + 1/3, -x + 2/3, z + 2/3$; #2 $-x + 1/3, -y + 2/3, -z + 2/3$; #3 $x - y, x, -z$; #4 $y, -x + y, -z$; #5 $-y + 2/3, x - y + 1/3, z - 2/3$.

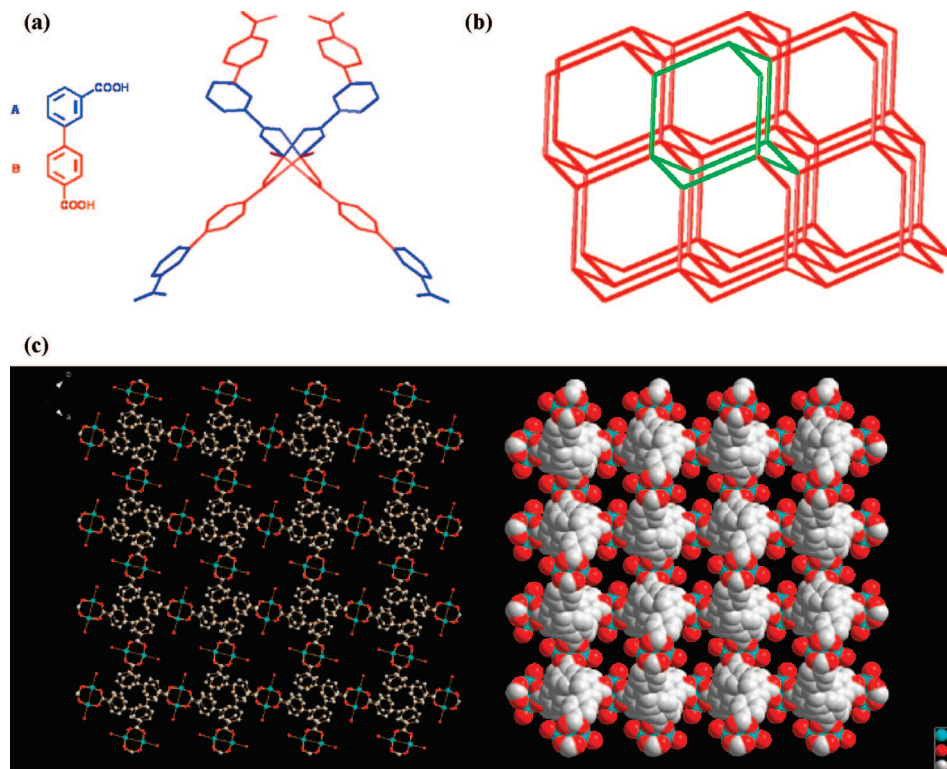


Figure 1. (a) The A–A–B–B coordinated arrangement of 3,4'-bpdc in structure 1. (b) View of the diamond topology of 1. (c) View of the 3-D framework along the *c* axis, showing 1-D square channels with a pore diameter about 5.8 Å. Color code: Cu, blue; O, red; C, gray.

by the symmetrical carboxylic acids. Each Cu paddlewheel is linked with four neighboring units by biphenyl connectors in an opposite way to generate a three-dimensional (3-D) 3-fold interpenetrating framework. Considering the Cu paddlewheel

as four-connected nodes and the biphenyl groups as linkers, one set of the structure has a diamond topology with the vertex symbol of $(6_2.6_2.6_2.6_2.6_2.6_2)$ as shown in Figure 1b. In spite of the interpenetration, **1** still reveals 1-D square channels of 5.8

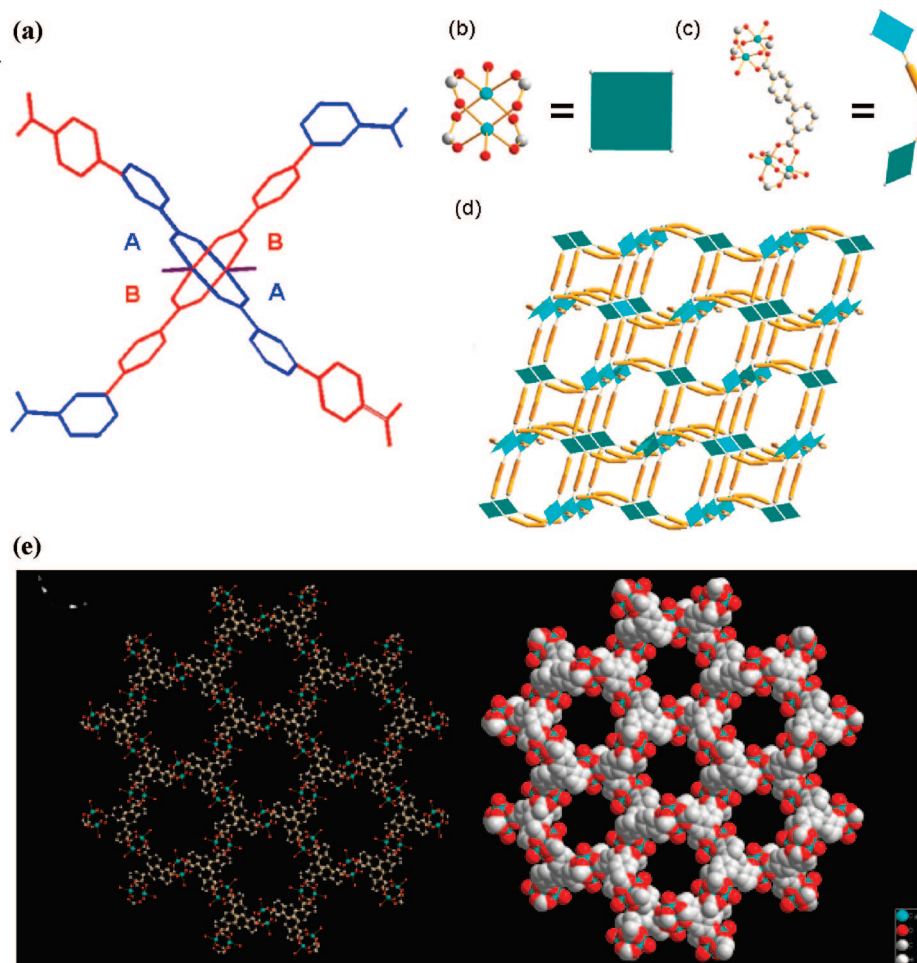


Figure 2. (a) The A–B–A–B coordinated arrangement of 3,4'-bpdc in structure **2**. (b) The $\text{Cu}_2(\text{CO}_2)_4(\text{H}_2\text{O})_2$ paddle-wheel unit (blue, square SBU); (c) two square SBUs linked by the organic 3,4'-bpdc linker (yellow, rods with the appropriate angles); (d) square SBUs (blue) and rods linkers (yellow) form the NbO network. (e) View along the c axis showing hexagonal channels with a pore diameter about 10.5 Å in structure **2**. Color code: Cu, blue; O, red; C, gray.

Å viewed along the [001] direction. (The sizes are estimated by measuring the horizontal distances between the centers of opposite coordinated water oxygen atoms and considering the van der Waals radii of the atoms; hereafter, all dimensions are reported in this way (Figure 1c).) In the as-prepared crystal of **1**, the solvent molecules are disordered within the pores. By elemental analysis and thermogravimetric analysis (TGA), the guest molecules in **1** were established to be two H_2O and one DMF molecules. Their contributions to the X-ray diffraction patterns were estimated by using PLATON/SQUEEZE.^{29,30} By PLATON/SOLV analysis, the accessible void in the desolvated structure of **1** was estimated to be 47.2% (2005.6 Å³ of the unit cell volume 4247 Å³).

Compound **2** crystallizes in hexagonal space group $R\bar{3}$, and the Cu(II) local coordination geometry is similar to that in **1**. Pairs of Cu(II) centers also form a paddle-wheel $[\text{Cu}_2(\text{O}_2\text{CR})_4]$. Different from **1**, the two carboxyl groups on the 3-position and two carboxyl groups the 4'-position adopt a central-symmetrical A–B–A–B arrangement (Figure 2a). The average Cu–O_c distance and Cu–O_w distance are 1.961(3) Å and 2.161(6) Å, respectively, which are also similar to those MOFs possessing a Cu paddle-wheel. The carboxylate groups are nearly coplanar with the corresponding linking phenyl rings (the dihedral angles between the carboxylate groups and phenyl ring are 3.3° and 5.4°, respectively), and the two phenyl rings have a twisting dihedral angle of 35.4°, indicating that the ligand in

structure **2** is less distorted than that in structure **1**. The 4-connected square paddle-wheel SBU (Figure 2b) was linked by the bidentate bridging ligand 3,4'-bpdc (Figure 2c) to form a 2-fold interpenetrating 3-D framework. One set of the structure has a NbO topology with the vertex symbol of (6₂.6₂.6₂.6₂.8₂.8₂) (Figure 2d). Viewing along the [001] direction, structure **2** reveals a large 1-D hexagonal channel with the pore diameter of 10.5 Å (Figure 2e). The disordered solvent molecules in **2** were established to be 4.5 H_2O and two DMF molecules by elemental analysis and TGA. The effective free volume of **2** is estimated by PLATON/SOLV analysis as 61.8% of the total volumes.

The symmetrical carboxylate ligands, such as 3,3'-bpdc^{33,34} and 4,4'-bpdc,³⁵ usually link metal atoms into ordered paddle-wheel units, resulting in 2-D layer structures due to the small dihedral angle between two phenyl rings. A second ligand such as pyridine derivatives is necessary to link the layers into 3-D frameworks. By using an unsymmetrical substituted rigid carboxylate ligand, 3,4'-bpdc as organic linker, 3-D supramolecular isomers **1** and **2** with network structural differences are obtained. Compared with the symmetrical carboxylate ligands, the carboxylate groups in the different positions have more coordinated arrangements, including A–A–B–B and A–B–A–B, which results in diversities of novel structures. In **1**, the noncentral symmetrical A–A–B–B arrangement leads to an uncommon twisted Cu-paddlewheel SBU, which favors a

tetrahedral configuration to form the diamond topology. However, the four carboxylates in structure **2** are coordinated with Cu in a central symmetrical A–B–A–B arrangement. The carboxylate groups are nearly coplanar with the Cu–Cu axis and corresponding linking phenyl rings, resulting in the 3-D NbO network, which was identified as the default structure for the assembly of square-planar 4-connected nodes where the square nodes are orthogonal.^{36–38} We believed that the minor differences of the carboxylate groups in two positions contribute to the structural differences of polymorphs **1** and **2**.

Thermogravimetry. Thermogravimetric analysis for **1** and **2** in atmosphere at a heating rate of 10 °C min^{−1} was performed on crystalline samples. For compound **1**, TGA (Figure S2, Supporting Information) shows that 25.7% over 25–218 °C corresponds to the liberation of two H₂O and one DMF guest molecule (calculated 25.3%), and then the coordinated water molecule begins to be lost at 218 °C with a weight loss of 4.3% (calculated 4.2%). The weight loss of 51.2% from 269 to 500 °C corresponds to the loss of one ligand 3,4'-bpdc (calculated 52.0%). Compound **2** shows a similar thermal stability; at the first step it loses 4.5 H₂O and two DMF guest molecules over 25–245 °C with a weight loss of 41.3% (calculated 41.4%). The coordinated water molecule begins to be lost between 245 and 269 °C with a weight loss of 3.3% (calculated 3.3%). From 269 to 500 °C, the ligand 3,4'-bpdc was lost with a weight loss of 40.9% (calculated 40.8%).

N₂ Adsorption. To confirm the permanent porosity, N₂ sorption measurements were performed at 77 K. The samples were immersed in acetone for 24 h to remove the guest solvates (DMF and H₂O). Before the measurement, the samples were activated at 120 °C under a vacuum for 12 h. The nitrogen sorption isotherm of **1** (Figure 3a) shows typical type I sorption behavior with a BET surface area of 541 m²/g and a pore volume of 0.22 cm³/g. The Horvath–Kawazoe (HK) model indicates a pore diameter of ca. 5.7 Å, which is consistent with the X-ray analysis. The isotherm shows an interesting hysteretic character, corresponding to the dynamic feature of the 3-fold interpenetrating frameworks. Although the crystal structure of **2** contains solvent accessible volume, it exhibits no sorption by all means, which may be due to the framework collapse after removing the solvents.

H₂ Adsorption. The high-pressure hydrogen adsorption of **1** and **2** were evaluated at 77 K. The samples were activated by the procedure described above in Experimental Section. The H₂ sorption isotherms of both complexes show type I behavior with no hysteresis and no noticeable change in properties upon repeated cycling. At 10 bar, **1** and **2** showed a gravimetric H₂ uptake of 2.26 and 1.64 wt %, which corresponds to a H₂ storage capacity of 251.1 mL·g^{−1} and 182.2 mL·g^{−1} (Figure 3b). Although the hydrogen uptake of **1** and **2** are lower than some MOFs reported with high hydrogen storage (such as MOF-505³¹ and UCM-150²¹), to our knowledge the hydrogen uptake of **1** is comparable with many MOFs such as [Ni-(cyclam)(bpydc)] of 1.8 wt%³⁹ and MOF-74 of 2.3%.⁴⁰

Conclusion

By using an unsymmetrical-substituted rigid carboxylate ligand, 3,4'-bpdc as organic linker, supramolecular isomers Cu(3,4'-bpdc)(H₂O)·DMF·2H₂O (**1**) and Cu(3,4'-bpdc)(H₂O)·2DMF·4.5H₂O (**2**) with network structural differences have been synthesized under mild solvothermal conditions. The strategy of using unsymmetrically substituted linker to build MOFs exhibits special superiority in the construction of polymorphs comparing with highly symmetrical linkers. By ad-

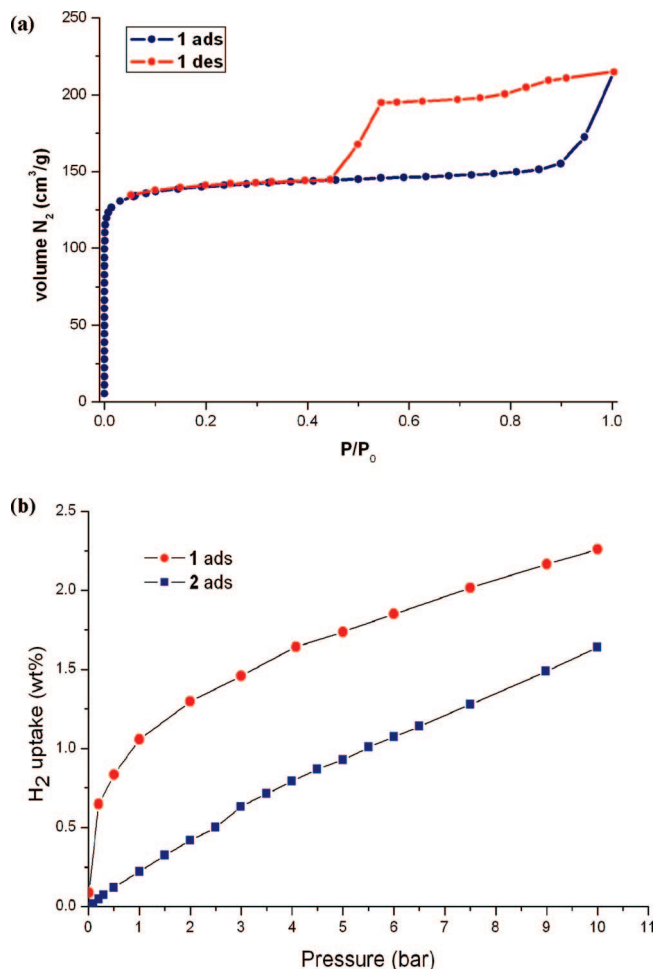


Figure 3. (a) N₂ sorption isotherms measured for desolvated **1** at 77 K, (b) H₂ sorption isotherms measured for desolvated **1** and **2** at 77 K.

justing the coordinated arrangements of carboxylate groups in different positions, structures **1** and **2** show diamond and NbO topologies, respectively. Besides their interesting structures, both of them possess larger 1-D channels and show the ability to adsorb H₂.

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Supporting Information Available: PXRD and TGA plots for compounds **1** and **2**; X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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