Single-crystal to single-crystal transformation from a hydrophilic–hydrophobic metal–organic framework to a layered coordination polymer

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ABSTRACT

A new metal–organic framework (MOF) $[Cu_5(pz)_2(\mu_3\text{-}OH)_2(bdc)_2(Hbdc)_2]\cdot 8H_2O$ (**1**) possessing both hydrophobic and hydrophilic channels has been prepared by two synthetic methods which have subtle differences. Interestingly, **1** can reversibly transform to a layered coordination polymer $Na\{[(Cu_3(pz)_3(\mu_3\text{-}OH)]_2(bdc)_2(Hbdc)\}\cdot DMF\cdot 21H_2O$ (**2**) upon a single-crystal to single crystal (SCSC) process. **1** exhibits an 8-connected three-dimensional (3D) framework constructed by pentanuclear copper units and bdc linkers, while **2** shows a two-dimensional (2D) network built by triangular trinuclear copper units and bdc linkers. Furthermore, the magnetic properties of both **1** and **2** have been studied.

1. Introduction

Metal–organic frameworks (MOFs) are of great contemporary interest not only because of their intriguing variety of architectures and topologies, but also their extensive applications in gas storage, catalysis, separation, ion-exchange and drug delivery [1,2]. Recently, single-crystal to single-crystal (SCSC) transformations that occur in MOFs have received considerable attention due to their importances for the development of new and useful materials including devices and sensors [3]. Moreover, during the course of SCSC transformation, the changes in the framework structure are accompanied by many interesting changes in properties such as host–guest behavior, magnetism, and photochemical reactivity, which help gain insights into the correlation between structure and property [4]. The driving forces of SCSC transformations of MOFs include light, heat, guest removal, uptake or exchange and chemical oxidation [5–8]. However, the researches on the SCSC transformations of MOFs are still limited since it is difficult for crystals to retain single crystallinity after the solid-state rearrangement of atoms.

The porous properties including pore size, shape and interior environment of MOFs are vital for their applications in gas storage, catalysis, separation, ion-exchange and drug delivery [9]. Biporous MOFs especially the ones with two kinds of pores strikingly differ in properties, such as one is hydrophobic while the other is hydrophilic, may show interesting selective adsorption and separation behaviors different from the MOFs with uniform pores [10,11]. Although their interesting properties and promising applications, only limited examples of MOFs possessing both hydrophobic and hydrophilic pores have been known. In 2010, Long and co-workers reported a MOF possessing both hydrophobic and hydrophilic pores constructed by face-sharing Keplerate-type heterometal–organic polyhedra [10a]. In 2011, Morris' group prepared a hydrophilic-hydrophobic MOF based on copper ions and monoesterified 1,3,5-benzenetricarboxylate linkers, which displayed switchable pore-discriminating adsorption properties [10b]. For the design and synthesis of MOFs, the large number of available organic linkers, offer not only the potential for the construction of structurally diverse MOFs but also the opportunity to create functionalized porous frameworks with the functional species (atoms or groups) projecting into the pore space [12]. And the current studies on MOFs have indicated that choosing suitable organic linkers, one linker with both hydrophobic and hydrophilic groups or mixed linkers system containing ligands with opposite polarity, is very critical for the achievement of MOFs possessing both hydrophobic and hydrophilic pores [11,13].

At the present work, we are trying to design and synthesize new hydrophilic-hydrophobic MOF by using the mixed ligands system

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composed of pyrazole (Hpz) and 1,3-benzenedicarboxylic acid (H$_2$bdc). Fortunately, from this mixed ligands system, one hydrophilic-hydrophobic MOF based on pentanuclear copper(II) units, [Cu$_5$(pz)$_2$(μ_3-OH)$_2$(bdc)$_2$(Hbdc)$_2$]·8H$_2$O (**1**), was successfully prepared. Interestingly, **1** can transform into a layered coordination polymer Na{[(Cu$_3$(pz)$_3$(μ_3-OH)]$_2$(bdc)$_2$(Hbdc)}·DMF·21H$_2$O (**2**) upon a SCSC process (details in Crystal-to-Crystal Transformation).

2. Experimental

2.1. Materials and methods

All the chemicals were obtained from commercial sources, and were used without further purification. All the reactions and manipulations were carried out in air. Elemental analyses (C, H, and N) were measured on a Perkin–Elmer 2400 CHN elemental analyzer; Cu and Na were determined with a Plasma-SPEC(I) ICP atomic emission spectrometer in a JEOL JEM 2010-F TEM (200 kV) equipped with a high resolution pole piece. IR spectra were performed in the range 4000–400 cm^{-1} using KBr pellets on an Alpha Centaurt FT/IR spectrophotometer. Thermogravimetric analyses (TGA) of the samples were performed using a Perkin–Elmer TG-7 analyzer heated from room temperature to 600 °C under N$_2$ at the heating rate of 5 °C min^{-1}. Variable temperature magnetic susceptibilities were measured with a MPMS-7SQUID magnetometer. Powder X-ray diffraction measurements were recorded radiation ranging from 3° to 50° at room temperature on a Siemens D5005 diffractometer with Cu Kα (λ = 1.5418 Å).

2.2. Syntheses

2.2.1. Synthesis of compound **1**

Method 1: A mixture of Cu(NO$_3$)$_2$·3H$_2$O (0.15 g, 0.6 mmol), Hpz (0.068 g, 1.0 mmol), H$_2$bdc (0.025 g, 0.15 mmol), methanol (2.5 mL) and DMF (2.5 mL) was stirred for 10 min in air with 10% sodium hydroxide solution to control the pH 5, then transferred to and sealed in a 15 mL Teflon-lined autoclave, heated in an oven to 110 °C for 48 h. The resulting blue block crystals were filtered, washed with DMF, and dried in air (21% yield based on bdc). Elemental *Anal.* Calc. for C$_{38}$H$_{42}$Cu$_5$N$_4$O$_{26}$: C, 35.42; H, 3.29; N, 4.35. Found: C, 35.08; H, 3.25; N, 4.31%. ICP analysis showed that **1** contained 24.52% Cu (calcd: Cu, 24.66%). IR (KBr, cm^{-1}): 3394s, 1656s, 1605s, 1559s, 1477s, 1440s, 1380s, 1272m, 1180m, 1159m, 1099m, 1079m, 1050s, 822w, 748s, 722s, 662m, 623w, 530w, 445m.

Method 2: A mixture of Cu(NO$_3$)$_2$·3H$_2$O (0.15 g, 0.6 mmol), Hpz (0.068 g, 1.0 mmol), H$_2$bdc (0.025 g, 0.15 mmol), methanol (2.5 mL), DMF (2.5 mL) and H$_2$O (2.5 mL) was stirred for 10 min in air with 10% sodium hydroxide solution to control the pH 5, then transferred to and sealed in a 15 mL Teflon-lined autoclave, heated in an oven to 110 °C for 48 h. The resulting blue block crystals were filtered, washed with DMF, and dried in air.

2.2.2. Synthesis of compound **2**

When the crystals of **1** and Hpz ligand were remained in their mother solution (in method 1) at room temperature for one day, block crystals of **1** transformed into similarly colored plate crystals of **2**. The crystals were filtered and washed with DMF, and dried in air. Elemental *Anal.* Calc. for C$_{45}$H$_{82}$Cu$_6$N$_{13}$NaO$_{36}$: C, 30.27; H, 4.63; N, 10.20. Found: C, 30.06; H, 4.58; N, 10.17%. ICP analysis showed that **2** contained 21.11% Cu and 1.27% Na (calcd: Cu, 21.36; Na, 1.29%). IR (KBr, cm^{-1}): 3615w, 3067w, 2924m, 2807w, 1700s, 1648s, 1607s, 1563s, 1490m, 1437s, 1379s, 1278m, 1255m, 1177m, 1096m, 1055s, 1021w, 966w, 831w, 747s, 723s, 662m, 637w, 530w, 453w.

2.3. X-ray crystallographic study

X-ray diffraction data, collected from a single crystal mounted atop a glass fiber with a Siemens SMART-CCD diffractometer, were corrected for Lorentz and polarization effects. The structures were solved employing the SHELXTL-direct methods program and refined by full-matrix least-squares methods on F^2 using the SHELXTL 97 crystallographic software package and anisotropic thermal parameters were used to refine all non-hydrogen atoms. The SQUEEZE program was used to estimate the solvent accessible voids and rest possible solvent molecules in the structure. Based on the calculation result, elemental analysis and TG analysis, another 8 H$_2$O and 21 H$_2$O were added directly in the final molecular formula of compound **1** and **2**, respectively. A summary of key crystallographic information and selected bond lengths and angles for **1** and **2** were given in Table 1, Tables S1 and S2.

3. Results and discussion

3.1. Structure description

3.1.1. Crystal structure of compound **1**

Single crystal X-ray diffraction analysis reveals that **1** crystallizes in the *P*4(2)/*m* space group and displays an 8-connected three-dimensional (3D) porous framework constructed from pentanuclear copper(II) units and bdc linkers. In **1**, there are two crystallographically independent copper atoms (Cu1 and Cu2). The pentanuclear copper unit is composed of a rectangular arrangement of four copper (Cu1) atoms and a centered fifth copper (Cu2) atom. The central Cu2 atom lies on a crystallographic inversion center, and therefore, the five copper atoms are coplanar (Fig. 1a). Each Cu1 atom is five-coordinated in a distorted square pyramidal geometry with one nitrogen atom from pyrazole ligand, one μ_3-OH group, and three carboxyl oxygen atoms from three different bdc ligands, while the central Cu2 atom adopts an octahedral coordination with two μ_3-OH groups and four carboxyl oxygen atoms from four different bdc ligands. For each bdc ligand, the two carboxylate groups show two distinct coordination modes: one is tridentate coordination mode bridging two Cu2 atoms at the long edge of the rectangular Cu$_4$ unit with central Cu1 atom, the

Table 1
Crystal data and structure refinements for compounds **1** and **2**.

	1	**2**
Formula	C$_{38}$H$_{42}$Cu$_5$N$_4$O$_{26}$	C$_{45}$H$_{82}$Cu$_6$N$_{13}$NaO$_{36}$
Formula weight	1288.46	1785.47
T (K)	293(2)	293(2)
Cryst size (mm^3)	0.28 × 0.24 × 0.24	0.28 × 0.24 × 0.21
Crystal system	tetragonal	triclinic
Space group	*P*4(2)/*m*	*P*$\bar{1}$
a (Å)	12.1998(17)	11.487(2)
b (Å)	12.1998(17)	19.660(4)
c (Å)	20.909(4)	20.550(4)
α (°)	90	63.47(3)
β (°)	90	86.35(3)
γ (°)	90	87.76(3)
V (Å^3)	3111.9(9)	4143.5(14)
Z	2	2
D_{calc} (g/cm^3)	1.375	1.431
F(000)	1302	1832
Data/restraints/parameter	2825/0/154	14205/42/730
μ (mm^{-1})	1.754	1.602
Goodness-of-fit on (GOF) F^2	1.012	1.046
R_1, wR_2 ($I > 2\sigma(I)$)[a]	0.0457, 0.1492	0.0656, 0.1427
R_1, wR_2 (all data)[a]	0.0556, 0.1551	0.1112, 0.1557
CCDC No.	963317	963316

[a] $R_1 = \sum ||F_0| - |F_c|| / \sum |F_0|$; $wR_2 = \sum [w(F_0^2 - F_c^2)^2] / \sum [w(F_0^2)^2]^{1/2}$.