



# Synthesis of chiral porous coordination polymer that shows structural transformation induced by guest molecules



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## ABSTRACT

We report the synthesis of a new chiral porous coordination polymer  $[Zn_2\{(R)-5,5'-BDA\}_2(dabco)]_n \cdot DMF$  (5,5'-BDA = 2,2'-dihydroxy-1,1'-binaphthalene-5,5'-dicarboxylic acid, dabco = 1,4-diazabicyclo[2.2.2]octane). This compound had one-dimensional (1D) channels which were occupied by DMF molecules. The hydroxyl groups on the surface of the channels acted as DMF interactive sites. Removal of DMF from the pores resulted in an amorphous solid. However, the apohost underwent a structural (amorphous-to-crystalline) transformation in response to the addition of guest molecules with amide groups. Interestingly, the observed degree of crystallinity was different for chiral amides, depending on the stereoisomer used.

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## 1. Introduction

Recently, porous coordination polymers (PCPs) or metal–organic frameworks (MOFs), which are built up from the self-assembly of metal ions with organic ligands, have emerged as a unique class of nanoporous materials [1–3]. Compared with conventional inorganic materials such as zeolites and activated carbons, PCPs can be synthesized in milder conditions, which allows the rational design of novel functional materials. PCPs have highly regular nanopores that can be utilized for gas storage, separation, sensing, ion transport, and polymerization [4–8]. A particularly interesting area in this field is the synthesis of homochiral PCPs and their potential applications, including enantioselective catalyst, separation, nonlinear optical, and ferroelectric properties [9–11].

One of the most reasonable strategies in designing homochiral PCPs is to combine a metal-containing nodes and chiral organic bridging ligands [12]. Tanaka et al. reported the synthesis of a two-dimensional (2D) chiral coordination polymer  $[Cu_2\{(R)-5,5'-BDA\}_2(H_2O)_2] \cdot MeOH \cdot 2H_2O$  (**1**; 5,5'-BDA = 2,2'-dihydroxy-1,1'-binaphthalene-5,5'-dicarboxylic acid) [13].

5,5'-BDA have axial chirality to form a chiral environment in frameworks. The 2D layers are stacked in an A-B-A sequence where the layers are offset, blocking open channels in the square grids. We took a so-called “pillaring strategy” to synthesize a 3D framework [14,15]. The structure of **1** shows paddlewheel coordination which consists of binuclear metal clusters in which two metal ions are bridged by four dianions to form a square-planar motif [16,17] (Fig. 1). Thus, coordination of appropriate pillar ligands to metal ions in the axial positions produces a 3D framework from **1**.

In this work, we describe the synthesis of a novel chiral PCP based on binuclear paddlewheel unit. For the construction of the porous framework, we employed two methods: the first approach is preparation of a 2D layer followed by mixing with 1,4-diazabicyclo[2.2.2]octane (dabco) as the pillar ligand (sequential reaction) [16]. The second approach is concurrent mixing of the metal ion, dabco, and (R)-5,5'-BDA (one-pot reaction) [13]. The synthesized PCP had 1D channels where hydroxyl groups were arranged and interacted with DMF molecules. Solvent exchange experiments indicated that guest molecules with an amide moiety could maintain the crystal structure of framework. Removal of DMF from the pores led to an amorphous solid. The amorphous-to-crystal transformation of dehydrated PCP was invoked by chiral molecules with an amide bond. Interestingly, the degree of crystallinity was changed, depending on which stereoisomer was used.

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## 2. Experimental

### 2.1. Materials

All reagents and chemicals used were obtained from commercial sources, unless otherwise noted. 5,5'-BDA, **1**, and methyl D-pyrroglutamate were prepared according to previously described methods [13,18]. <sup>1</sup>H NMR, <sup>13</sup>C NMR, IR, and ESI-MS data of 5,5'-BDA and methyl D-pyrroglutamate were included in Supplementary material.

### 2.2. Measurement

Single-crystal X-ray diffraction measurement was performed at 283 K with a Rigaku AFC10 diffractometer with Rigaku Saturn Kappa CCD system equipped with a MicroMax-007 HF/VariMax rotating-anode X-ray generator with confocal monochromatized Mo K $\alpha$  radiation. Data were processed by a direct method (SIR97) and refined by full-matrix least-squares refinement using the SHELXL-97 computer program. The hydrogen atoms were positioned geometrically and refined using a riding model. X-ray powder diffraction (XRPD) data were collected on a Rigaku RINT 2000 Ultima diffractometer with Cu K $\alpha$  radiation. The infrared spectra were measured employing a Thermo Scientific Nicolet iS5. <sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained using a JEOL A-500 spectrometer operating at 500 MHz. The orbitrap mass spectrometer (Thermo Fisher Scientific) equipped with an ESI source was used.

### 2.3. Preparation

#### 2.3.1. Preparation of PCP with Cu<sup>2+</sup>

In the sequential reaction, 2D layer **1** was prepared in advance according to the published method [9]. Subsequently, **1** (44 mg, 0.09 mmol) were added to dabco (20 mg, 0.18 mmol) in mixed solvents of DMF (3.25 ml), MeOH (1.2 ml), and toluene (0.6 ml). The resulting mixture was heated under solvothermal condition at 140 °C for 8 h.

In the one-pot reaction, (R)-5,5'-BDA (100 mg, 0.27 mmol), Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (72 mg, 0.42 mmol), and dabco (28 mg, 0.25 mmol) were added together to mixed solvents of DMA (2.0 ml), and MeOH (3.0 ml). The resulting mixture was heated under solvothermal condition at 135 °C for 48 h.

#### 2.3.2. Preparation of PCP with Zn<sup>2+</sup>

(R)-5,5'-BDA (744 mg, 2.0 mmol), Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (304 mg, 1.0 mmol) and dabco (112 mg, 1.0 mmol) was added to DMF, and the slurry was stirred at room temperature for 5 h. After the white precipitate was filtered, the solution was heated at 100 °C for 2 days to afford single crystals [Zn<sub>2</sub>{(R)-5,5'-BDA}<sub>2</sub>(dabco)<sub>n</sub>·DMF

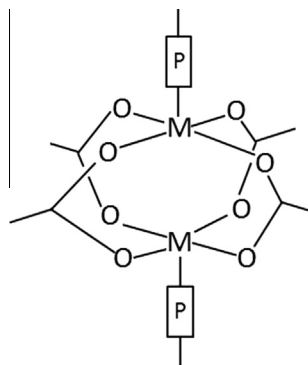


Fig. 1. Bimetal paddlewheel structure (P; pillar ligand).

(2-DMF) which were suitable for single crystal X-ray diffraction measurement (yield 78%). IR spectrum (cm<sup>-1</sup>): 2929, 1665, 1622, 1575, 1557, 1506, 1464, 1436, 1387, 1255, 1220, 1173, 1150, 1092, 1059, 1017, 924, 839, 815, 785.

### 2.4. Guest exchange

2-DMF was immersed in a variety of solvents, such as dimethylacetamide (DMA), dimethylacrylamide (DMAA), acetone, acetonitrile, chloroform, 2-propanol, methanol, tetrahydrofuran (THF), benzene, and toluene. The mixture was left for 3 h, replacing the solvent with fresh one every 1 h.

### 2.5. X-ray crystallography

The data was treated with the SQUEEZE routine in PLATON to correct reflection intensities, corresponding to disordered solvent molecules. Crystal data of [Zn<sub>2</sub>{(R)-5,5'-BDA}<sub>2</sub>(dabco)<sub>n</sub>·DMF (**2-DMF**)] are summarized in Table 1. Further crystallographic details for the structure reported in this paper can be obtained from the Cambridge Crystallographic Data Center ([www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html)), E-mail: deposit@ccdc.cam.ac.uk) on quoting the depository numbers CCDC 1007454 for **2-DMF**.

## 3. Results and discussion

### 3.1. Synthesis and description of crystal structure

The axial sites of Cu<sub>2</sub> paddlewheel units in **1** are occupied with MeOH and/or H<sub>2</sub>O molecules. Thus, 3D frameworks can be synthesized by insertion of proper pillar ligands at the axial sites. We synthesized 2D layer **1**, and then exchanged with dabco at the axial position of Cu<sup>2+</sup> ions by a heterogeneous reaction between **1** and dabco following the sequential method. After heating **1** and dabco in mixed solvents, a green powder was obtained. We compared the XRPD pattern of the green powder with that of [Cu<sub>2</sub>(4,4'-biphenyldicarboxylate)<sub>2</sub>(dabco)<sub>n</sub> (**3**) to confirm the crystal structure of the product [19]. The distance between the carboxyl group at 1 and 4 positions of (R)-5,5'-BDA was similar to that of 4,4'-biphenyldicarboxylic acid. Therefore, the product was expected to have the almost identical structure to **3**. In fact, the

Table 1  
Crystal data and structure refinement of **2-DMF**.

Chemical formula	C <sub>31</sub> H <sub>32</sub> N <sub>3</sub> O <sub>8</sub> Zn
Formula mass	639.98
Crystal system	tetragonal
<i>a</i> (Å)	21.441 (5)
<i>b</i> (Å)	21.441 (5)
<i>c</i> (Å)	9.655 (2)
$\alpha$ (°)	90.00
$\beta$ (°)	90.00
$\gamma$ (°)	90.00
Unit cell volume	4438.56
Temperature (K)	283
Space group	<i>P</i> 4 <sub>2</sub> /2
No. of formula units per unit cell, <i>Z</i>	4
No. of reflections measured	72 144
No. of independent reflections	2939
<i>R</i> <sub>int</sub>	0.071
Final <i>R</i> <sub>1</sub> values [ <i>I</i> > 2σ( <i>I</i> )] <sup>a</sup>	0.086
Final w <i>R</i> ( <i>F</i> <sup>2</sup> ) values [ <i>I</i> > 2σ( <i>I</i> )] <sup>b</sup>	0.228
Final <i>R</i> <sub>1</sub> values (all data)	0.095
Final w <i>R</i> ( <i>F</i> <sup>2</sup> ) values (all data)	0.234
Goodness-of-fit (GOF) on <i>F</i> <sup>2</sup>	1.509
Flack parameter	0.05 (3)

<sup>a</sup>  $R_1 = (|F_o| - |F_c|)/|F_o|$ .

<sup>b</sup>  $wR_2 = [w(F_o^2 - F_c^2)]/w(F_o^2)^{1/2}$ .

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