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 $[\text{Zn}_2\{(\text{R})\text{-5,5'-BDA}\}_2(\text{dabco})]_n \cdot \text{DMF}$ (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.

Keyword: porous coordination polymer; paddlewheel; chiral recognition

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 materials¹⁻³. 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 polymerization⁴⁻⁸. 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 properties⁹⁻¹¹.

One of the most reasonable strategies in designing homochiral PCPs is to combine a metal-containing nodes and chiral organic bridging ligands¹². Tanaka et al reported the synthesis of a two-dimensional (2D) chiral coordination polymer $[\text{Cu}_2\{(\text{R})\text{-}5,5'\text{-BDA}\}_2(\text{H}_2\text{O})_2]\cdot\text{MeOH}\cdot 2\text{H}_2\text{O}$ (**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-diazacyclo[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.

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} ¹H-NMR, ¹³C-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 α 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 CuK α radiation. The infrared spectra were measured employing a Thermo Scientific Nicolet iS5. ^1H and ^{13}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^{2+}

In the sequential reaction, 2D layer **1** was prepared in advance according to the published method⁹. Subsequently, **1** (44mg, 0.09mmol) were added to dabco (20mg, 0.18mmol) in mixed solvents of DMF (3.25ml), MeOH (1.2ml), and toluene (0.6ml). The resulting mixture was heated under solvothermal condition at 140 °C for 8 hours.

In the one-pot reaction, (R)-5,5'-BDA (100mg, 0.27mmol), $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (72mg, 0.42mmol), and dabco (28mg, 0.25mmol) were added together to mixed solvents of DMA (2.0ml), and MeOH (3.0ml). The resulting mixture was heated under solvothermal condition at 135 °C for 48 hours.

2.3.2 Preparation of PCP with Zn^{2+}

(R)-5,5'-BDA (744mg, 2.0mmol), $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (304mg, 1.0mmol) and dabco (112mg, 1.0mmol) was added to DMF, and the slurry was stirred at room temperature for 5 hours. After the white precipitate was filtered, the solution was heated at 100 °C for 2 days to afford single crystals $[\text{Zn}_2\{(\text{R})\text{-5,5'-BDA}\}_2(\text{dabco})]_n \cdot \text{DMF}$ (**2**·DMF) which were suitable for single crystal X-ray diffraction measurement (yield 78 %). IR spectrum (cm^{-1}): 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 hours, replacing the solvent with fresh one every 1 hour.

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 $[\text{Zn}_2\{(\text{R})\text{-5,5'-BDA}\}_2(\text{dabco})]_n \cdot \text{DMF}$ (**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, 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 Cu₂ paddlewheel units in **1** are occupied with MeOH and/or H₂O 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 Cu²⁺ 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 [Cu₂(4,4'-biphenyldicarboxylate)₂(dabco)]_n (**3**) to confirm the crystal structure of the product¹⁹. 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 product showed a peak at $2\theta = 5.6^\circ$, corresponding to the diffraction peak of **3** at $2\theta = 5.8^\circ$ which was likely derived from (100) plane (Fig. S1). However, because of the low crystallinity of the product, we could not identify the exact crystal structure. For the determination of dabco incorporated into the framework, we measured solution ¹H-NMR after dissolving the product in 0.05M Na₄-EDTA deuterium oxide. ¹H-NMR spectrum of the solution indicated that the mole ratio of dabco to carboxylic linker was 0.1 which was smaller than the ideal ratio of 0.5. The insertion of dabco between the layers might be difficult probably because of the strong interlayer packing. The small amount of pillar ligand would result in the low crystallinity.

Next, we attempted to synthesize the PCP by the one-pot reaction, however, heating a DMF solution of all components together also gave a low crystalline product. Crystallinity of compounds could not be improved by changing the experimental conditions, such as temperature (110 °C – 160 °C) and solvent (MeOH, toluene, DMF, and DMA).

Zn ions can form a paddlewheel unit, hence, pillared-layer type PCPs with an identical structure to that of the Cu ion can be synthesized from Zn ion²⁰. In addition, due to the mild Lewis acidity, Zn ions form a weak coordination bond with ligands, which would allow slow kinetics of nucleation and crystal growth²¹. To obtain a single crystal with high purity we conducted the one-pot reaction of Zn ion, (R)-5,5'-BDA, and dabco.

Here we heated DMF solution of Zn(NO₃)₂, 5,5'-BDA, and dabco. The solution was left at 100 °C for 2 days, giving the crystalline product [Zn₂{(R)-5,5'-BDA}₂(dabco)]_n·DMF (**2**·DMF). The structure of **2**·DMF could be determined by single-crystal X-ray diffraction. The framework of **2** is composed of binuclear Zn₂ units with a paddle wheel structure, which are bridged by (R)-5,5'-BDA dianions to form a undulating 2D layer [Zn₂{(R)-5,5'-BDA}₂] with a cavity of dimensions 8.0 × 14.0 Å (Fig. 3). The DMF molecules are trapped to hydroxyl moieties of (R)-5,5'-BDA in the

cavities ($\text{O(DMF)}\text{--O(hydroxyl)} = 2.5 \text{ \AA}$). As expected, the axial sites of the Zn_2 paddle wheels are occupied by dabco, which act as pillars to extend the 2D layers into a 3D structure with 1D channel along the c-axis. XRPD pattern of bulk prepared sample were very similar to the simulated one based on single-crystal structure, ensuring the high phase purity (Fig. 2).

3.2. Structural transformation

In the nanochannels of **2**, DMF molecules interact with the hydroxyl groups, which are highly ordered on the surface of the channels. To evaluate the interaction between DMF and hydroxyl groups, we carried out IR measurements of **2**·DMF in a region corresponding C=O stretching of DMF. Compared with neat DMF ($\nu_{\text{C=O}} = 1675 \text{ cm}^{-1}$), DMF accommodated in the channels of **2** showed clear peak shifts toward lower wavenumber ($\nu_{\text{C=O}} = 1665 \text{ cm}^{-1}$), because of a hydrogen bond formation between carbonyl group of DMF and hydroxyl group of **2** (Fig 4).

Removal of DMF by heating **2**·DMF at $130 \text{ }^\circ\text{C}$ for 15 hours under reduced pressure resulted in the amorphous state. The XRPD patterns for the amorphous compound (**2'**) are shown in Fig 2. This crystalline-to-amorphous transformation is accompanied by a loss of DMF molecules in the channels. However, when **2'** was immersed in DMF, it reverted to the original crystalline phase **2**, which is observed by XRPD measurement (Fig 2). This transformation did not occur in the other solvents without amide groups (acetone, chloroform, and MeOH), which suggests the formation of hydrogen bonds between guest and host is an important key to determine amorphous-to-crystalline transformation.

We investigated the guest-dependence on the structural transformation behavior. **2**·DMF was immersed in various solvents to exchange DMF molecules. After filtration, the adducts were dissolved in 0.05M $\text{Na}_4\text{-EDTA}$ deuterium oxide. $^1\text{H-NMR}$ measurements of the solutions ensured quantitative exchange of DMF molecules ($< 1\text{wt}\%$). XRPD measurements showed that DMA and dimethylacrylamide (DMAA), both having an amide group could maintain the structure of **2**, in contrast, acetone, acetonitrile, chloroform, 2-propanol, MeOH, tetrahydrofuran, benzene, and toluene collapsed or changed the structure of **2** (Fig. S2). The obtained results suggested that guest molecules that have an amide moiety stabilized the structure through hydrogen bonding.

3.3. Chiral recognition

Addition of methyl D- and L-pyroglutamate with amide moiety (Fig. 5) to **2'** led to the original XRPD patterns of **2**. Interestingly, a difference in the peak intensity was observed between **2**·D-isomer and **2**·L-isomer. The crystallinity of **2**·D-isomer seemed to be higher, comparing with that of **2**·L-isomer (Fig. 6). The degree of crystallinity was estimated to be 15.9 % for **2**·D-isomer and 3.2 % for **2**·L-isomer using the background subtraction method in Materials Studio²² (Fig. S3).

Recognition of chiral molecules plays an important role in the production of wide range of pharmaceuticals, agricultural chemicals²³. Chiral PCPs have attracted considerable attention because of their potential applications in chiral recognition^{9,10,24}. It was demonstrated that chiral recognition

of PCPs was attributed to the difference of accessibility of a chiral molecule to the interaction sites between D- and L-isomer by single crystal X-ray diffraction measurement²⁴. Due to the chirality of **2** derived from 5,5'-BDA, we presumed that the amorphous-to-crystalline transformation was affected by which stereoisomer was used.

4. Conclusion

We successfully synthesized a novel chiral porous coordination polymer, $[\text{Zn}_2\{(\text{R})\text{-}5,5'\text{-BDA}\}_2(\text{dabco})]_n \cdot \text{DMF}$ (**2**·DMF), from the one-pot reaction of all components. The crystal structure of **2**·DMF was identified by single crystal X-ray diffraction measurement. The hydroxyl groups, which were highly ordered on the surfaces of the channels, interacted with DMF molecules. After removal of DMF molecules, **2** was changed to the amorphous solid (**2'**) that underwent a structural (amorphous-to-crystalline) transformation in response to the incorporation of guest molecules with an amide moiety. In addition, the degree of crystallinity of **2** after the structural transformation was different between D- and L-isomer. We expect that this study can provide insights into new rational design strategies for PCPs with chiral recognition.

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Chemical formula	C ₃₁ H ₃₂ N ₃ O ₈ Zn
Formula mass	639.98
Crystal system	tetragonal
a (Å)	21.441 (5)
b (Å)	21.441 (5)
c (Å)	9.655 (2)
α (°)	90.00
β (°)	90.00
γ (°)	90.00
Unit cell volume	4438.56
Temperature (K)	283
Space group	<i>P</i> 4 ₂ /2
No. of formula units per unit cell, Z	4
No. of reflections measured	72144
No. of independent reflections	2939
R _{int}	0.071
Final R ₁ values (<i>I</i> > 2σ(<i>I</i>)) ^a	0.086
Final wR(F ²) values (<i>I</i> > 2σ(<i>I</i>)) ^b	0.228
Final R ₁ values (all data)	0.095
Final wR(F ²) values (all data)	0.234
Goodness of fit (GOF) on F ²	1.509
Flack parameter	0.05(3)

^a $R_1 = (|F_o| - |F_c|) / |F_o|$.

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

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

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

Fig. 2. XRPD patterns of simulated **2** (black), as-synthesized **2** (red), **2'** (blue), and **2'** after immersing in DMF (green).

Fig. 3. (a) Coordination environment of Zn ion and (b) top view and (c) side view of **2**·DMF. Legend: Zn: green, O: red, C: grey, N: blue. DMF molecules are omitted for clarity.

Fig.4. IR spectra of carbonyl group of DMF in **2** (red) and neat (black).

Fig. 5. Molecular structures of methyl pyroglutamate (D-isomer; left, L-isomer; right).

Fig. 6. XRPD patterns of **2** (black), **2**·L-isomer (red), and **2**·D-isomer (blue).

Graphical Abstract (Pictogram)

Synthesis of Chiral Porous Coordination Polymer that Shows Structural Transformation Induced by Guest Molecules

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