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Dynamic Coordination Polymers with 4,4′-Oxybis(benzoate): Reversible Transformations of Nano- and Nonporous Coordination Frameworks Responding to Present Solvents

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Reversible construction of a nanoporous framework from a nonporous framework has been found in the zinc(II) coordination polymer with 4,4′-oxybis(benzoate) (oba). $[Zn_2(oba)_2(dmf)_2]\cdot2DMF$ (**1**), which has 1 nm scale channels, transforms to the nonporous coordination polymer $[Zn(oba)(H_2O)]$ (**2**) with the loss of the open framework. Compound **2** on treatment with DMF reversibly yields nanoporous compound **1**.

Coordination polymers with porous frameworks have attracted attention as a new class of porous materials because these materials have shown new porous functions that are not found in inorganic porous materials such as zeolites and graphite.[1−7] For example, heterogeneous catalysis,[2] anion exchange,[3] and molecular adsorption and storage[4] have been reported to date. Their frameworks are unstable and flexible in many cases, and various new functions based on the dynamic porous frameworks have been created.[5−8] One of the recent interests in this field is the reversible transformation between a nanoporous framework and a nonporous framework accompanying the release and readsorption of guest molecules responding to external stimuli.[5,6,8] For example, Pan et al. have reported a recyclable nanoporous coordination framework that changes to a nonporous framework by addition of water with loss of a pillar framework ligand, 4,4′-bipyridine (4,4′-bpy).[6] This reaction enforces the release of the included guest molecules. Moreover, treatment of the resulting nonporous framework with 4,4′-bpy in DMF at 150 °C reproduces the original porous framework.

We have focused on the synthesis of new coordination networks with chalcogen atoms in the organic backbone.[8a,9] Recently, we selected 4,4′-oxybis(benzoate) (oba; Scheme 1) as a bridging ligand for creation of new coordination frameworks, and we have succeeded in the synthesis of the two new coordination polymers: nanoporous coordination polymer, $[Zn_2(oba)_2(dmf)_2]\cdot2DMF$ (**1**) and $[Zn(oba)(H_2O)]$

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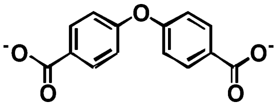
Scheme 1



oba

(**2**). Here, we report the synthesis, structures, and the unique dynamic structural changes that reversibly transform their frameworks, depending on the solvents, with loss and recreation of the porous framework.

The nanoporous coordination polymer **1** was obtained as highly moisture-sensitive colorless crystals by the reaction of $Zn(CH_3COO)_2{\cdot}2H_2O$ with H_2oba in dry DMF,[10] and characterized by single crystal X-ray analysis.[11] As shown in Figure 1, **1** has a two-dimensional framework, which is constructed by connections of dinuclear zinc units with oba ligands. Although the network motif is similar to those of $[Cu_2$(1,4-benzenedicarboxylate$)_2]$[4b] and $[Zn_2$(1,4-benzenedicarboxylate$)_2$(dmf$)_2]$,[4d] the bent oba structure provides a new unique structural aspect in the channel shape and thickness of the layer. That is, the oba ligand is largely bent at the ether-oxygen sites (C−O−C = 121.8(4)°), causing an undulation along the *c*-axis. As a result, the cavity shape deviates from a regular square to a rhombus with size of about 17 Å × 13 Å along the two diagonal directions. The bent structure of oba also contributes about 11 Å of the thickness of the layer, in which ether-oxygen sites of oba remarkably stick out from the plane.

Despite the large cavities, these layers stack along the *b*-axis without interpenetration. The thickness of the layer could inhibit the possibility of interpenetration. As shown in Figure 1b, **1** creates nanoscale channels along the *b*-axis. The channel size is about 13 Å × 9 Å, which is slightly contracted compared with the cavity size of each layer because of the slight alternate slides of the stacked layers (these two layers are illustrated as blue and red frameworks in Figure 1b). The channels are filled with two free DMF molecules per one dinuclear unit. We monitored the changes of the X-ray powder diffraction (XRPD) patterns of **1** under air to study the stability or dynamic property of the moisture-sensitive framework. This experiment demonstrated that **1** transforms to a new crystalline material via an amorphous state because of reaction with H_2O (a similar change was also induced by immersing **1** in water).

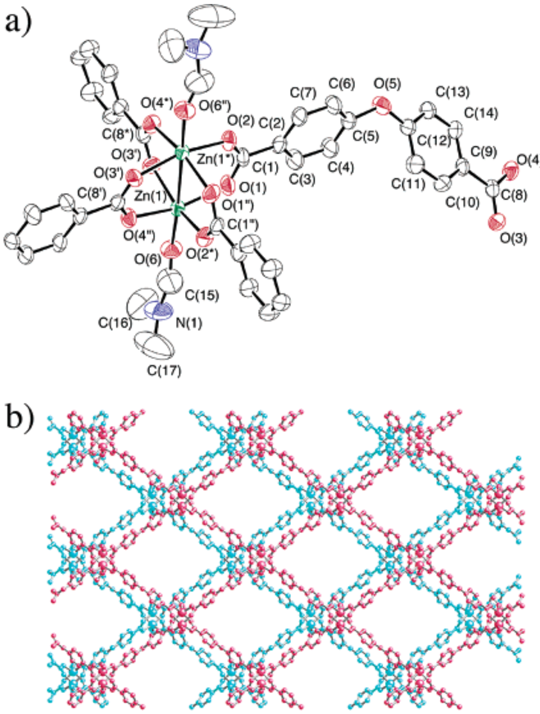


Figure 1. Structure of **1**. ORTEP view around the dizinc center (a) and the stacked aspect of the two-dimensional layers (b), in which alternate layers are shown by red and blue colors, respectively.

For the structural characterization of the product obtained from **1** and water, we prepared a new coordination polymer **2** from the aqueous reaction mixture of $Zn(NO_3)_2{\cdot}6H_2O$ and H_2oba in the presence of base.[12] We confirmed that **2** is a reaction product of **1** with H_2O by comparing the simulated XRPD pattern based on the atomic coordinates of **2** and the observed pattern of the obtained product (see Supporting Information).

The structure of **2** is shown in Figure 2,[11] in which the framework arrangement is similar to that of the previously reported [Cd(oba)(H_2O)].[13] Each Zn center forms a distorted trigonal bipyramid with four carboxylate oxygen atoms from oba and one water molecule. The two carboxylate moieties of the oba bridge each Zn center to produce one-dimensional $(Zn{-}oba)_n$ chains. These chains are further connected by the oba-frameworks to yield a two-dimensional structure. Similarly to **1**, these layers are not planar but undulated due to the bending at the ether-oxygen sites of the oba ligand. The coordinating waters between the layers form hydrogen bonds with the two carboxylate-oxygen atoms of the oba in the adjacent layer. As a result, a three-dimensional network is constructed.

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(10) Synthesis of **1** follows: A DMF solution (200 mL) of oba (5.2 g, 20 mmol) was allowed to diffuse into a DMF solution (200 mL) of $Zn(CH_3COO)_2{\cdot}2H_2O$ (2.2 g, 10 mmol). The colorless cubic crystals formed within 3 days were collected by filtration under N_2 atmosphere. Elemental analysis (%) calcd for $C_{40}H_{44}N_4O_{14}Zn_2$: C, 51.35; H, 4.74: N, 5.99. Found: C, 50.37; H, 4.69; N, 5.89.

(11) Crystal data for **1** follow: $C_{40}H_{44}N_4O_{14}Zn_2$, $M_r = 935.57$, orthorhombic, space group *Pnna* (No. 52), $a = 23.79(1)$ Å, $b = 15.887(7)$ Å, $c = 17.773(8)$ Å, $V = 6716(4)$ Å^3, $Z = 4$, μ(Mo Kα) = 0.759 mm^{-1}, $T = 293$ K, $R = 0.059$, $R_w = 0.063$ for 2951 unique reflections ($R_{int} = 0.061$) with $I > 2\sigma(I)$ and 246 parameters. Crystal data for **2** follow: $C_{14}H_{10}O_6Zn$, $M_r = 339.61$, monoclinic, space group $P2_1$ (No. 13), $a = 7.391(6)$ Å, $b = 6.273(5)$ Å, $c = 14.256(11)$ Å, $\beta = 103.572(10)°$, $V = 642.5(8)$ Å^3, $Z = 2$, μ(Mo Kα) = 1.937 mm^{-1}, $T = 293$ K, $R = 0.057$, $R_w = 0.065$ for 1660 unique reflections ($R_{int} = 0.028$) with $I > 2\sigma(I)$ and 101 parameters. The structural determinations for this system follow: The data for all the structures were measured on a Rigaku Mercury CCD system (Mo Kα radiation $\lambda = 0.71073$ Å). An empirical absorption correction was applied. The structures were solved by direct method (SIR92).[15] Non-hydrogen atoms were refined anisotropically, and the all hydrogen atoms were not refined but included.

(12) Synthesis of **2** follows: An aqueous solution (100 mL) of 4,4′-oba (1.49 g, 5 mmol) was allowed to diffuse into an aqueous solution of $Zn(NO_3)_2{\cdot}6H_2O$ (1.49 g, 5.0 mmol) and excess NEt_3. The colorless crystals obtained after 1 week were collected by filtration. Elemental analysis (%) calcd for $C_{14}H_{10}O_6Zn$: C, 49.51; H, 2.97. Found: C, 49.23; H, 3.18.

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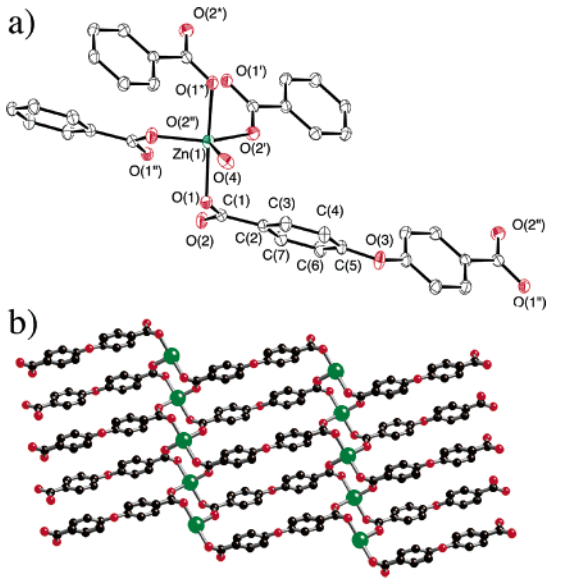

Figure 2. Structure of **2**. ORTEP view around the zinc center (a) and the two-dimensional network (b).

Despite the different framework structures, as mentioned above, **1** readily transforms to **2** by addition of water. Furthermore, we found that the reverse transformation, i.e., formation of **1** from **2**, also proceeds under mild conditions, i.e., by addition of DMF to **2** and standing for 3 days. These structural changes were monitored by the changes in the XRPD peaks, which are summarized in Figure 3. The XRPD peaks for **1** (Figure 3a) disappear within 20 min under air due to the change to an amorphous state (Figures 3b). After 1 day, the resulting powder shows a new XRPD pattern due to the formation of **2** (Figures 3c). Some drops of DMF solvent on the resulting powder reproduce XRPD peaks for **1** after 3 days (Figures 3d). Although crystal shape and size seem to be retained during the transformation between **1** and **2**, these processes are not single-crystal-to-single-crystal[7] but proceed via an amorphous state. Transformation from **2** to **1** could proceed by recrystallization process[4e,f,15] as Pan's system[6] despite the lower solubility (one piece of crystal of **2** is not dissolved in 100 mL of DMF). Neither structural transformation is induced by other general organic guests, such as benzene, dioxane, alcohols, THF, and acetonitrile, within a few weeks, demonstrating that these structural reconstitutions would be selectively induced by H_2O and DMF for **1** to **2** and the reverse transformation, respectively.

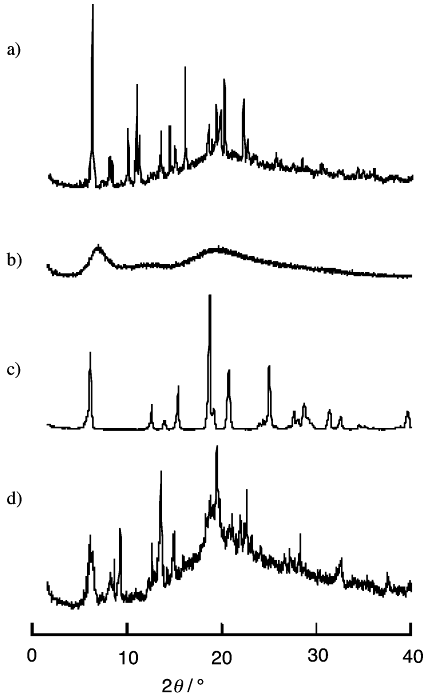

Figure 3. XRPD (Cu Kα) pattern of a fresh sample of **1** (a), which changes to amorphous material under air (b), followed by **2** (c). The original pattern for **1** was regained (d) after the addition of a few drops of dmf to **2**. The low intensities of the peaks of parts a and d are due to their high air sensitivity, which changes the structure to amorphous during the measurements.

Although a similar transformation has been reported by Pan et al.,[6] that system accompanies the loss of 4,4′-bpy upon formation of the nonporous framework; therefore, addition of 4,4′-bpy is necessary for recreation of the nanoporous framework under vigorous reaction conditions (150 °C in DMF for 3 days). In contrast, our system is superior in that the transformation proceeds under mild conditions without the addition or loss of the bridging ligands. Moreover, to the best of our knowledge, this is the first example that a nanoporous framework having channels larger than 10 Å is reversibly created from a nonporous framework. Our preliminary study reveals that the porous framework of **1** is not retained without guest molecules to yield amorphous material. Nevertheless, these dynamic channels would be useful for porous functions such as small molecule adsorption and heterogeneous catalysis in solution observed for many flexible coordination polymers.[1−3,5,8] Further studies of the functions based on this dynamic framework are in progress.

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Supporting Information Available: TG data of **1**, XRPD patterns of **2** with simulation, and X-ray crystallographic files for **1** and **2** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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