

# A Dynamic, Isocyanurate-Functionalized Porous Coordination Polymer\*\*

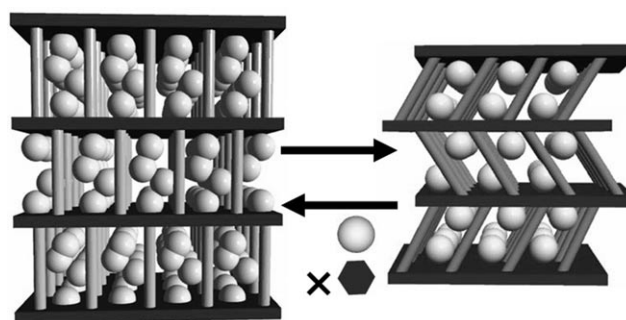
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Porous coordination polymers (PCPs) or metal–organic frameworks (MOFs) have attracted much attention due to scientific interest in the creation of nanometer-sized spaces and for their potential application in molecular sieves, gas storage, and heterogeneous catalysis.<sup>[1–4]</sup> Besides porosity, stability, and pore shape and size, pore-surface functionalization and framework flexibility are currently considered to be key factors for the next generation of PCPs.<sup>[1b,3–4]</sup> Some PCPs exhibit dynamic behavior and thus can be developed into unique classes of materials, such as highly selective gas sensors and gas-separating materials, which could not be obtained with rigid porous materials.

To functionalize the channel surface, two types of strategies are used: introduction of organic groups to provide guest-accessible functional organic sites (FOSs),<sup>[5]</sup> and immobilization of coordinatively unsaturated (open) metal sites (OMSs).<sup>[6]</sup> The use of OMSs for Lewis acid catalysis and specific gas adsorption has been widely explored in PCPs, but less attention has been devoted to FOSs despite their importance. This is because of the difficulty of producing guest-accessible FOSs on the pore surface, as organic groups tend to coordinate metal ions in a self-assembly process to give frameworks in which FOSs are completely blocked. In most cases framework flexibility results from coordinative bonds, H-bonds,  $\pi$ -electron stacking, and van der Waals interactions.<sup>[7]</sup> Ligands having a highly flexible component are another possibility which has not been commonly used to prepare three-dimensional (3D) PCPs.<sup>[6a]</sup>

Here we report the synthesis, structure, and selective (stepwise) sorption properties of two isomorphous 3D  $\text{Ln}^{\text{III}}$  frameworks, synthesized from a tripodal symmetrical ligand with a highly flexible arms ( $-\text{CH}_2\text{CH}_2-$ ) and secondary functional groups ( $-\text{C}=\text{O}$ ), which shows spongelike dynamic

behavior, directly visualized by single crystal to single crystal transformations (Scheme 1).

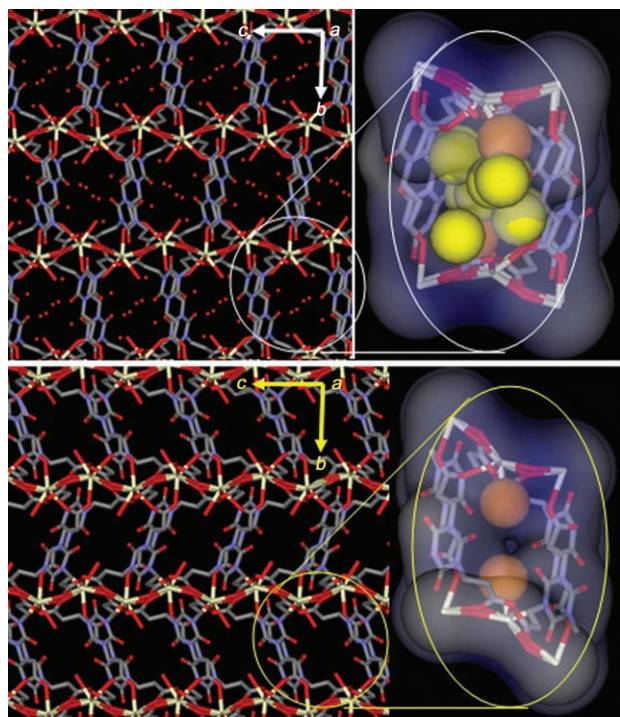


**Scheme 1.** Selective guest sorption by dynamic structural transformation of a soft coordination polymer.

Two isomorphous 3D porous coordination frameworks  $\{[\text{Ln}(\text{tci})\cdot\text{H}_2\text{O}]\cdot 4\text{H}_2\text{O}\}_n$  ( $\text{Ln} = \text{Ce}$  (**1**),  $\text{Gd}$  (**2**);  $\text{tciH}_3 = \text{tris}(2\text{-carboxyethyl})\text{isocyanurate}$ ) were obtained from  $\text{Ln}(\text{NO}_3)_3\cdot x\text{H}_2\text{O}$  and  $\text{tciH}_3$  by hydrothermal synthesis. Both compounds are stable in air and insoluble in common organic solvents. As both **1** and **2** are isomorphous, only the structure of **1** is described in detail herein. The asymmetric unit of **1** consist of one  $\text{tci}^{3-}$  unit, one  $\text{Ln}^{\text{III}}$  ion one metal-bound water molecule, and four free water molecules. Each metal ion exhibits ninefold coordination by two bidentate carboxylate units, four bridging carboxylate oxygen atoms from six different ligands, and one water molecule. All three carboxylate groups of the  $\text{tci}^{3-}$  unit are involved in bidentate chelation of  $\text{Ln}^{\text{III}}$ , and two of them also form bridges with another  $\text{Ln}^{\text{III}}$  ion to extend the framework. These bridging bonds form metal carboxylate chains along the  $c$  axis. Three arms of the ligand bridge three such metal carboxylate chains, and this continuous network forms the assembled 3D structure (see the Supporting Information). In simpler terms, the metal carboxylate chains are bridged by two arms of the tripodal ligand to form a 2D sheet structure, and these 2D sheets are bridged by the third arm of the ligand to generate a porous 3D structure (Figure 1). The resultant 3D framework contains 1D channels ( $2.85 \times 2.74 \text{ \AA}$ ;  $V_{\text{void}} = 21.1\%$  of the total crystal volume)<sup>[8]</sup> along the crystallographic  $a$  axis, occupied by four water molecules, which are H-bonded with the carbonyl groups of the ligand, the coordinated water molecule, and the carboxylate oxygen atoms. The water molecules inside the channels are highly disordered. After determining the structure, the simulated powder X-ray diffraction (XRD) pattern was found to match those of as-synthesized compounds **1** and **2**. The stepwise thermogravi-

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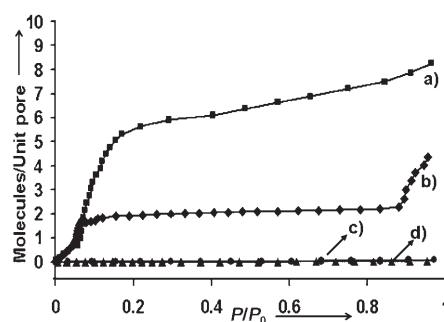
**Figure 1.** Perspective views of the 3D dynamic frameworks of as-synthesized **1** containing water-filled 1D channels along the *a* axis (top) and partially dehydrated framework **1a** (bottom), with close-up views of the inner surface of the channel for both the frameworks. (C gray, N blue, O red, Ce light yellow/white; free and coordinated water molecules are shown as yellow and orange balls, respectively; H atoms are omitted for clarity.)

metric (TG) profile of **1** indicates that the four guest water molecules are released below 100 °C, and the single coordinated water molecule is released at about 150 °C. The compound is stable up to about 300 °C, above which it decomposes gradually, possibly because of cleavage of the coordinative bonds of the ligands (see the Supporting Information). Thus, partially dehydrated phase **1a** with one coordinated water molecule can be obtained by heating at a temperature below 100 °C, and the fully dehydrated compound above 150 °C. The powder XRD pattern of **1a** indicates that the framework maintains good crystallinity, but the fully dehydrated compound is not crystalline, that is, the 3D framework can not persist after removal of the coordinated water molecules.

It is noteworthy that compound **1** retains its single-crystallinity even after removal of the guest water molecules by heating the crystals at 70 °C for about 7 h under an Ar atmosphere. The single-crystal X-ray structure of the partially dehydrated crystal (**1a**) revealed that the compound shrinks, largely along the *b* axis, but the original crystal symmetry is retained. Due to the very flexible  $-\text{CH}_2\text{CH}_2-$  parts of the ligand, the framework can easily make adjustments along all the directions with available free space to form the required structure. The cross section of the one-dimensional channels shrinks from  $2.85 \times 2.74 \text{ \AA}$  to  $2.52 \times 1.30$ , and the void space in **1a** is 13.2% as opposed to 21.1% in **1**. The structural transformation changes the cross-sectional shape along the

*a*-axis from pseudosquare in **1** to parallelogram in **1a** (Figure 1). The structural changes occur mainly by movement of the flexible arms of the ligand. When the dehydrated single crystal of **1a** was exposed to the ambient atmosphere for 1–2 d, single-crystal cell measurement revealed that it had returned to the original structure **1**, that is, the dynamic structural transformation is reversible.

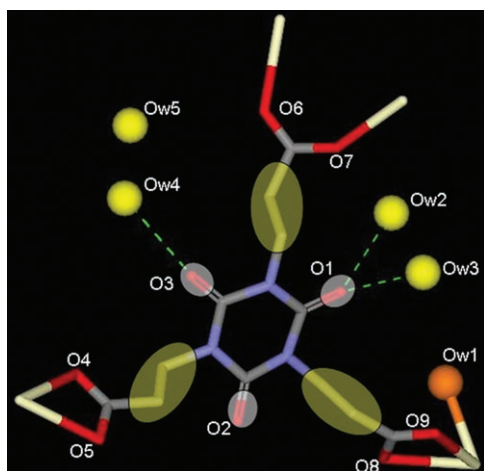
Since the completely dehydrated phase of the framework is not stable, we carried out sorption measurements on partially dehydrated phase **1a**. Adsorption of  $\text{CO}_2$  at 195 K and  $\text{N}_2/\text{O}_2$  adsorption at 77 K show only surface adsorption (see the Supporting Information). Interesting phenomena were observed in solvent sorption experiments at 298 K (Figure 2). In the case of  $\text{H}_2\text{O}$  as guest, **1a** absorbs four water



**Figure 2.** Adsorption profile of a)  $\text{H}_2\text{O}$  (squares), b) MeOH (diamonds), c) MeCN (circles), and d) EtOH (triangles) of **1a** at 298 K.

molecules which correspond to eight water molecules per unit pore, as in **1**. The sorption profile initially increases slowly, with a value at  $P/P_0 \approx 0.06$  that corresponds to one  $\text{H}_2\text{O}$  molecule per unit pore, and then increases very fast. This indicates that water molecules can not easily enter the small pores ( $2.52 \times 1.30 \text{ \AA}$ ), but H-bonding interactions of the pore surface with the water molecules enable the guests to enter the pores. Like water molecules, MeOH molecules ( $3.80 \times 4.70 \text{ \AA}$ ) also can not easily enter the small aperture of the channel ( $2.52 \times 1.30 \text{ \AA}$ ). Two MeOH molecules entered per unit pore. One molecule of MeOH ( $P/P_0 \approx 0.05$ ) entered with slow rise of the curve, the then curve rose rapidly with absorption of another MeOH molecule per unit pore, and became saturated until, at high pressure ( $P/P_0 \approx 0.9$ ), the profile showed another sharp increase, which may be due to the adsorption in the spaces between the particles of the compound. The  $\text{H}_2\text{O}$  and MeOH molecules strongly interact with the surface, and therefore desorption becomes very difficult and shows a hysteresis profile. In the pore surface with the four carbonyl groups of the ligand the two coordinated  $\text{H}_2\text{O}$  molecules of the controlled structure of the partially dehydrated phase also increase the hydrophilic nature. Interestingly, despite the comparable size of acetonitrile ( $3.80 \times 5.49 \text{ \AA}$ ) to methanol, it can not enter the channels, which may be due to the fact that MeOH can form strong H-bonds with the hydrophilic pore surface which helps it to enter the pore, but MeCN can not and thus fails to enter the pore. The above findings are also supported by the crystal structure of compound **1a**: the close-up of the channel

(Figure 1) shows that four oxygen atoms (two each of O1 and O3) of the FOSs ( $\text{C}=\text{O}$  groups) of the ligand are directed towards the channel pore and are completely free to form strong H-bonds, as in the case of **1** (Figure 3), in which H-bonds are formed directly with the guest water molecules



**Figure 3.** Perspectives view of H-bonding of the FOSs (carbonyl groups in white circles) of the ligand with guest water molecules in **1**. Flexible parts ( $-\text{CH}_2\text{CH}_2-$ ) of the ligand are indicated by yellow ellipses. (C gray, N blue, O red, Ce light yellow; free and coordinated water molecules are shown as yellow and orange balls, respectively; H atoms are omitted for clarity.)

(Ow2, Ow3, and Ow4). The combined effects of both ligand flexibility and affinity of guests for the FOSs in the pore surface is responsible for such dynamic behavior. The initial slow rise of the absorption profile in the low-pressure region arises from the strong affinity of guest molecules toward the pore surface within the very small channel aperture ( $2.52 \times 1.30 \text{ \AA}$ ). Ingress of guest molecules is also supported by the flexible parts of the ligand by expanding the pore aperture size with an increase in crystal-cell volume of about 14%, as shown by single crystal to single crystal transformations between **1** and **1a**. Other guest molecules which are very large size compared to the channel aperture, such as EtOH, THF, and  $\text{Me}_2\text{CO}$ , are not adsorbed, and therefore it is clear that selectivity arises from the very small size of the channel window in comparison to the size of the adsorbates.

In conclusion, we have synthesized two isomorphous soft 3D porous crystals with hydrophilic channel surfaces by using a flexible ligand with secondary functional groups. The framework shows size- and affinity-based selective sorption by means of dynamic structural changes, visualized by analysis of single crystal to single crystal structural transformation.

## Experimental Section

Single crystals of **1** and **2** were prepared by reaction of  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  and tris(2-carboxyethyl)isocyanurate ( $\text{tc}(\text{H}_3)$ ) in 15 mL of water by the hydrothermal technique.

X-ray powder diffraction was carried out on a Rigaku RINT-2000 Ultima diffractometer with  $\text{CuK}\alpha$  radiation. TG analyses were

performed on a Rigaku Thermo plus TG 8120 apparatus. The adsorption isotherms of  $\text{H}_2\text{O}$ , MeOH, MeCN, and EtOH at 298 K were measured with BELSORP18 volumetric adsorption equipment from Bel Japan, and the low-temperature adsorption isotherm for gases was determined with a Quantachrome AUTOSORB-1.

X-ray structural data for all structures were collected on a Rigaku Mercury CCD diffractometer with graphite-monochromated  $\text{MoK}\alpha$  radiation ( $\lambda = 0.71069 \text{ \AA}$ ). All structures were solved by direct methods using SHELXTL<sup>[9]</sup> and refined on  $F^2$  by full-matrix least-square techniques using the SHELXL-97<sup>[10]</sup> program package. CCDC-666786 (**1**), 666787 (**1a**) and -666788 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

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