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Framework Materials

Reversible Topochemical Transformation of a Soft Crystal of a Coordination Polymer**

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One of the goals of materials chemistry is the synthesis of crystalline compounds known as porous coordination polymers (PCPs) or metal-organic frameworks (MOFs) that are built from organic ligands and metal ions.[1] Their frameworks are composed of a variety of structures ranging from one-dimensional (1D), 2D, to 3D motifs depending on how the coordination bonds form. These compounds, which are low-density solids, can be tailored, and have potential use in gas storage, molecular sensing, and other materials applications. One of the most important discoveries in the area of PCPs is their flexible and dynamic properties, which are characteristic of the cooperative action of organic and inorganic moieties.[2,3] Guest-responsive changes between the solid phases are particularly intriguing. Although various cases of structural transformation (single crystal to amorphous phase) are known, examples of single-crystal to single-crystal phase (SCSC) transformation[4–6] are still lacking. A low-dimensional (1D or 2D) framework has a structural freedom in regards to the metal ions, while a 3D framework is sufficiently rigid to prevent recombination of the coordination bonds around the metal ions. As the structures and properties of SCSC structural transformations are well characterized, they are highly suitable for study to gain a further understanding of their dynamic behavior. In particular, structural transformations involving 2D and 3D frameworks are most important because most of the coordination compounds with important properties—such as gas storage, separation, sensor, magnetism, and catalysis—are generally 3D frameworks, whereas 2D structures containing spaces between the layers have more dynamic properties. The exploration of such a transformation is significant because it can provide not only unique properties characteristic of 3D frameworks, but also external stimulus-responsive properties based on the 2D–3D transformation (Figure 1).

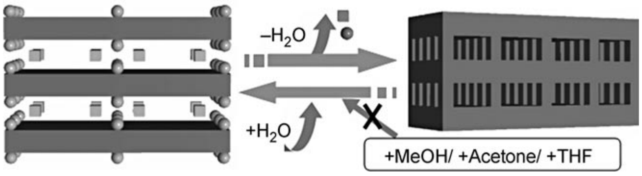

Figure 1. Schematic representation of the SCSC transformations from a 2D to a 3D nonporous framework triggered by a specific guest. Joining the plates represents the formation of the new bonds.

Herein, we describe the synthesis of a 2D compound using tetramethylammonium chloride as a blocking agent[7] (to stop the formation of the 3D structure), a tridentate ligand having highly flexible arms, and lanthanide metal ions, which have variable and high coordination numbers, which can provide more structural freedom to facilitate the transformation to a 3D structure.

Two isomorphous compounds, $\{[Ce(tci)(H_2O)_2]\cdot 2H_2O\}_n$ (**1**) and $\{[Pr(tci)(H_2O)_2]\cdot 2H_2O\}_n$ (**2**), were prepared by the hydrothermal technique using tris(2-carboxyethyl) isocyanurate ($tciH_3$) with $Ln(NO_3)_3\cdot xH_2O$ in the presence of tetramethylammonium chloride. The compounds once formed are insoluble in most solvents, including H_2O. The structure of **1** is shown in Figure 2. The asymmetric unit consists of one Ce^{III} center, one molecule of tci, and two types of H_2O molecules—two bound to Ce ions and two free in the channel. Each Ce^{III} ion is surrounded by eight oxygen atoms, two of the oxygen atoms being from the water molecules and the rest come from the tci unit to give an overall distorted square-antiprismatic geometry around the metal center. The metal ions and the carboxylate groups of the ligand form metal–carboxylate chains with alternate Ce⋯Ce distances of 4.414 Å and

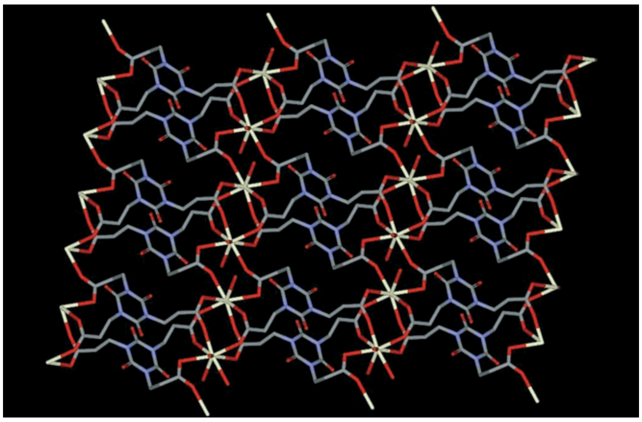

Figure 2. 2D sheet structure of **1** (as synthesized). Color code for all figures: carbon: gray, nitrogen: blue, oxygen: red, cerium: light yellow.

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4.742 Å, and these chains are joined to the other metal–carboxylate chains of the same sheet through the core ring of the tci with its three flexible arms. The distances between the corresponding metal centers of the next metal–carboxylate chain of the same sheet is 12.430 Å. The closest metal⋯metal distance in the adjacent layers is 8.661 Å (Figure 3).

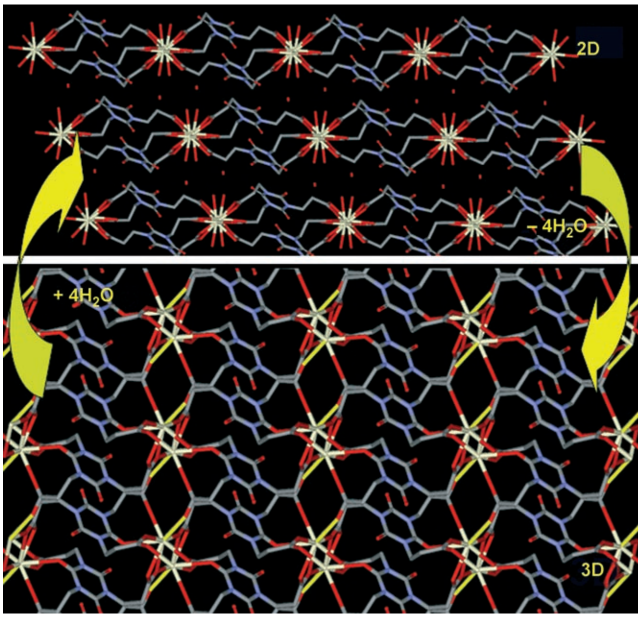
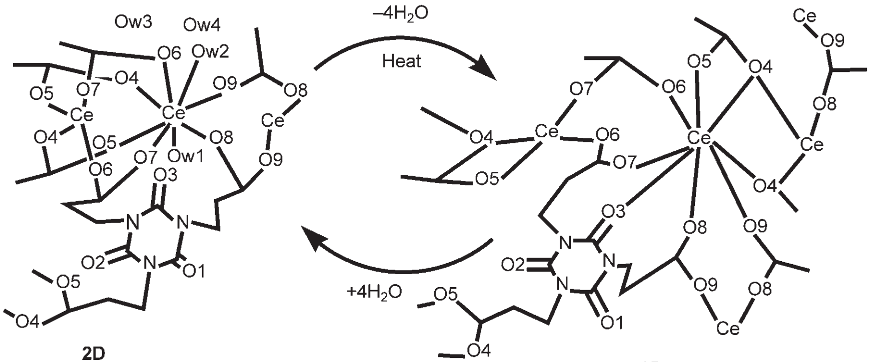


Figure 3. Perspective view of the reversible transformation between the 2D layer structure of **1** (as synthesized) and the 3D structure of **1′** (dehydrated). New bonds between the sheets are shown in yellow.

Thermogravimetric analysis (TGA) of compounds **1** and **2** revealed that it lost all the H_2O molecules above 140 °C, with a mass loss of approximately 13 % (calculated loss of 12.9 % for **1** and 12.9 % for **2**), and with no further loss up to 300 °C. The X-ray powder diffraction (XRPD) pattern of the bulk compounds **1** and **2** matched the simulated patterns (see Figure S6 in the Supporting Information), thus showing the phase purity of the compound, which was also confirmed by elemental analysis for both compounds. When **1** was heated at 150 °C for 5 h it lost all the H_2O molecules, as confirmed by TGA. The XRPD pattern of the dehydrated sample $\{Ce(tci)\}_n$ (**1′**) shows that the compound is still crystalline, but the pattern is different from that of the original compound **1**. To monitor the change of structure by diffraction, one frame of the single-crystal diffraction of compound **1** was monitored at different time intervals under continuous heating at 80 °C. This approach shows clear changes in the diffraction pattern of the original crystal with time and the change to a completely new pattern, after which no changes were observed even after heating for a long time. The colorless crystal becomes opaque after dehydration. We collected data on the sample after the complete change of the diffraction pattern. Fortunately, we were able to determine the crystal structure of the dehydrated product **1′** (similar results were also obtained for compound **2**, but the data were not good enough to enable the structure to be solved). Interestingly, although the structure of the dehydrated product **1′** bears a close relationship to the as-synthesized compound **1** (same crystal symmetry), it results in a new structure with a 3D coordination framework (Figure 4). The 2D–3D SCSC transformation was not previously known in coordination polymers, the closest analogue being observed in some alkali metal/bismuth/selenium 2D slab compounds, where the topotactic redox coupling of the Se–Se bond between the layers was observed to make it 3D.[8] Compound **1′** is not porous, as can be seen from the crystal structure and also from adsorption measurements of CO_2 and N_2, which show no adsorption. After removal of the water molecules, the unit cell volume of the compound decreased by about 20 % from 886.9(8) for **1** to 716.8(7) for **1′**. The asymmetric unit of **1′** contains one tci ligand and one metal center. This structural change involved removal of the free (two) and coordinated (two) H_2O molecules. Drastic structural changes occurred during the transformation (Figure 3). Two bond rearrangements between the two metal centers, the breakage of two bonds, and the formation of two bonds make **1′** also octacoordinate (see Figure S4 in the Supporting Information), similar to **1**. The cleavage of two bonds (corresponding to coordinated H_2O molecules) and the formation of two new bonds (to O4 and O3) occurred with the rearrangement of two additional bonds from one metal center to the other (O5 and O9). The ligand's arms are very flexible because of the -CH_2CH_2- unit, and can easily move up and down relative to the central ring of the tci, thus allowing the large structural changes observed. A carboxylate oxygen atom (O9) is the key atom in the structural transformation from the 2D sheet to the 3D framework. The O9–Ce bond of one 2D sheet breaks and a bond reforms through coordination with the metal center of the next sheet, which leads to the formation of the 3D structure. The reversibility of the transformation has been supported by the TGA, XRPD, and single-crystal studies. When the dehydrated compound was kept at room temperature for three days it showed the



2D
$\{[Ce(tci)(H_2O)_2]\cdot 2H_2O\}_n$ (**1**)

3D
$\{[Ce(tci)]\}_n$ (**1′**)

Figure 4. Bonding rearrangements during the transformation.

same amount of H_2O loss by TGA measurements as did **1**, and the XRPD pattern changed to look similar to that of **1** with weak intensity, which is improved after keeping the sample under H_2O vapor. The cell parameters of the rehydrated compound (**1a**) measured after a few days of keeping the crystal of **1′** at room temperature showed the return of the compound to the original structure, with recovery of the partial transparency (see Figure S10 in the Supporting Information).

Like the as-synthesized compounds **1** and **2**, the dehydrated 3D compound **1′** is also very stable in the presence of other common solvents such as methanol, ethanol, tetrahydrofuran, and acetone, and shows two stable forms with different dimensions. The stability of the dehydrated compound **1′** against other solvents was studied by XRPD, which showed no change in the patterns after treating the dehydrated compound with solvents (see Figure S7 in the Supporting Information). The stability and lack of uptake of the solvents was also confirmed by TGA and solvent sorption measurements (MeOH used as a representative solvent). TGA showed that there was no weight loss after treating the dehydrated compound with methanol, and the same decomposition temperature as that of the dehydrated compound was observed (300–350 °C), which was also reconfirmed by the sorption study, thus showing there was no uptake of methanol. When **1′** was treated with H_2O vapor, the XRPD pattern expectedly changed back to that of the as-synthesized compound. The reabsorption of the same amount of water was also confirmed by TGA and by an adsorption study. The dehydrated compound can adsorb four H_2O molecules per formula unit, exactly the same amount as present in the as-synthesized compound (Figure 5). Interestingly the isotherm shows a gate-opening type profile, dissimilar to the usual Type-I adsorption, with an abrupt increase at a relative P/P_0 value of 0.12:1.

This onset pressure is referred to as the gate-opening pressure of the flexible porous frameworks.[3c] This feature is associated with the high affinity metal sites for water molecules, so-called guest-accessible metal sites. The compound has two phases, which are reversibly transformable with one another and can be triggered using a specific guest.

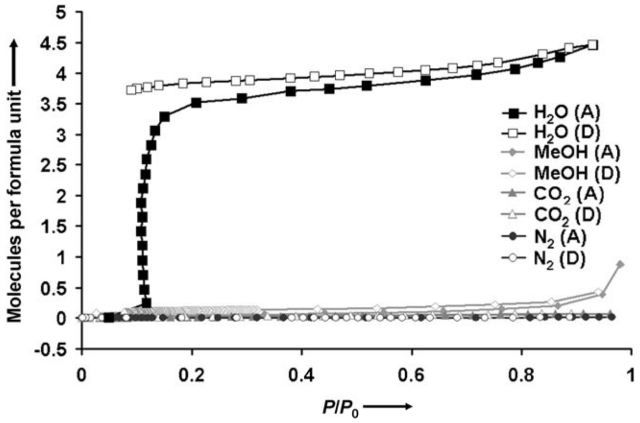


Figure 5. Adsorption (A) and desorption (D) isotherms of H_2O (RT), MeOH (RT), CO_2 (195 K), and N_2 (77 K) for **1′**.

In conclusion, we have synthesized two isomorphous flexible coordination polymers based on Ce^{III} and Pr^{III} ions by rationally choosing a flexible ligand that exhibits reversible SCSC transformations to form two different stable forms with a change in dimension from a 2D sheet to a 3D framework, which can be controlled by specific guests. The dehydrated compounds can selectively adsorb H_2O molecules and reject other adsorbates such as methanol, ethanol, acetone, tetrahydrofuran, nitrogen, carbon dioxide. The flexible frameworks are under investigation to determine the change in other properties in the different stable forms.

Experimental Section

1: A single crystal of **1** was prepared by treating $Ce(NO_3)_3{\cdot}6H_2O$ (1 mmol), tris(2-carboxyethyl) isocyanurate ($tciH_3$; 1 mmol), and tetramethylammonium chloride (2 mmol) in water (10 mL) by the hydrothermal technique in a teflon-lined autoclave. The autoclave was heated under autogenous pressure to 150 °C for 3 days and then cooled to RT over 24 h. Upon cooling the mixture to RT, the desired product appeared as long colorless rectangular parallelopipeds in ca. 60 % yield. Elemental analysis (%) calcd for $C_{12}H_{20}N_3O_{13}Ce$ (554.43): C 25.99, H 3.63, N 7.58 %; found: C 25.70, H 3.49, N 7.72 %.

2: Compound **2** was synthesized by using the same method as for **1**, but using $Pr(NO_3)_3{\cdot}6H_2O$ instead of $Ce(NO_3)_3{\cdot}6H_2O$. Yield ca. 60 %. Elemental analysis (%) calcd for $C_{12}H_{20}N_3O_{13}Pr$ (555.22): C 25.96, H 3.63, N 7.56 %; found: C 25.57, H 3.52, N 7.67 %.

X-ray structure determination of **1**, **1′**, and **2**: Data were collected on a Rigaku Mercury CCD diffractometer with graphite monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71069$ Å). All the structures were solved by direct methods using SHELXTL[9] and refined on F^2 by the full-matrix least-square technique using the SHELXL-97[10] program package. Crystal data for **1**: $C_{12}H_{20}N_3O_{13}Ce$, triclinic, space group $P\bar{1}$, $a = 9.113(2)$, $b = 9.368(2)$, $c = 12.430(4)$ Å, $\alpha = 100.362(5)$, $\beta = 102.570(4)$, $\gamma = 115.681(5)°$, $V = 886.9(8)$ Å^3, $Z = 2$, $T = 213$ K, $R = 0.0723$, $wR_2 = 0.1779$, GOF = 1.065. Crystal data for **2**: $C_{12}H_{20}N_3O_{13}Pr$, triclinic, space group $P\bar{1}$, $a = 9.119(2)$, $b = 9.328(2)$, $c = 12.411(3)$ Å, $\alpha = 100.428(6)$, $\beta = 102.612(5)$, $\gamma = 115.769(7)°$, $V = 880.9(9)$ Å^3, $Z = 2$, $T = 213$ K, $R = 0.0539$, $wR_2 = 0.1337$, GOF = 1.043. Crystal data for **1′**: $C_{12}H_{12}N_3O_9Ce$, triclinic, space group $P\bar{1}$, $a = 8.655(2)$, $b = 9.159(2)$, $c = 10.603(3)$ Å, $\alpha = 98.560(4)$, $\beta = 98.183(6)$, $\gamma = 117.337(5)°$, $V = 716.8(7)$ Å^3, $Z = 2$, $T = 353$ K, $R = 0.1139$, $wR_2 = 0.2645$, GOF = 1.052. Crystal cell data for **1a**: $a = 9.077(2)$, $b = 9.432(3)$, $c = 12.552(4)$ Å, $\alpha = 100.322(4)$, $\beta = 101.949(6)$, $\gamma = 114.889(5)°$, $V = 884.56(8)$ Å^3, $T = 213$ K. CCDC-652332 (**1**), CCDC-652333 (**1′**), and CCDC-652334 (**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.

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