Metal–Organic Frameworks

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Organic Cation and Chiral Anion Templated 3D Homochiral Open-Framework Materials with Unusual Square-Planar {$M_4(OH)$} Units**

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Microporous materials find applications primarily as shape- or size-selective adsorbents, ion exchangers, and catalysts.[1] The recent progress in the synthesis of new crystalline microporous materials with novel compositional and topological characteristics promises new and advanced applications.[2] For example, homochiral open-framework materials are of current interest owing to their potential applications in asymmetric catalysis and enantioselective separation.[3]

The original zeolite synthesis relies on the use of simple inorganic cations such as Na^+ as extraframework guest species, and a small number of new porous materials such as zeolite A have been made with this inorganic-templating method.[1] One of the most important contributing factors for the diversity of crystalline microporous materials now known is the use of charged organic templates (also called structure-directing agents, most commonly tetraalkylammonium cations or protonated cationic amines) to direct the self-assembly of molecular precursors (almost always achiral) into extended frameworks.[4] Such a combined charge- and space-templating method has been employed for the synthesis of porous materials in a wide range of chemical compositions such as aluminosilicate zeolites and microporous aluminophosphates, resulting in the discovery of novel materials (for example, ZSM-5) with important industrial applications and economic impact.[1]

In comparison with the above materials with inorganic frameworks, there have been much fewer examples of 3D covalent metal–organic frameworks (MOFs), homochiral inorganic–organic hybrids in particular, that are templated with charged organic species. Some examples of homochiral MOFs templated with charged organic species include those prepared from ionic liquids whereby cations of the ionic liquid are encapsulated in the resulting MOFs.[5] With few exceptions, known 3D homochiral metal–organic frameworks built from enantiopure chiral molecular precursors usually have neutral frameworks and sometimes cationic frameworks that are charge-balanced with simple inorganic anions.[6] Obviously, a synthetic approach that allows the self-assembly of enantiopure chiral molecular precursors into extended frameworks templated by charged organic templates will help to significantly expand the diversity of metal–organic homochiral solids, in a way similar to the impact of charged organic molecules on the synthesis of aluminosilicate zeolites, microporous phosphates, and many other inorganic open-framework materials. One limitation of cation- or anion-templated materials is the removal of extraframework species, which tends to be more difficult than the removal of neutral solvent molecules.

The work reported herein presents interesting examples of the synthesis of homochiral metal–organic framework materials templated by charged organic species. In addition to the zeolite-like templating method by protonated cationc amines, we also demonstrate a rare example of metal–organic frameworks templated by an enantiopure anionic template. Furthermore, we show an unusual structural building unit: the square-planar {$M_4(OH)$}$^{7+}$ ($M = Cd^{2+}$, Co^{2+}). It is worth noting that such coordination geometry is rather unusual for both metal cations (Cd^{2+} or Co^{2+}) and anionic O^{2-}, because even though the μ_4-OH ligand is known in the literature,[7] it tends to be with other metals and is not in a square-planar geometry. The utility of such organically templated syntheses is also shown here by the range of topological nets obtained: four-connected, six-connected, and eight-connected framework topologies are all accessible.

A total of five new organically templated homochiral open frameworks (compounds **1**–**5**) based on D-camphoric acid (D-H_2cam) are reported here (Table 1). Compound **1** was synthesized hydrothermally while **2**–**5** were made solvothermally by employing mixed organic solvents. These materials exhibit three distinct topological types: enantiopure anion templated twofold interpenetrating diamond net (crystal **1**), homochiral body-centered cubic (bcu) net based on unusual eight-connected square {$M_4(OH)$} units (crystals **2**, **3**, **4**), and a six-connected net (crystal **5**).

Compound **1** is an unusual metal–organic framework material templated by an enantiopure anionic template (Figure 1). In contrast to numerous metal–organic framework materials containing carboxylates, the enantiopure D-Hcam monoanions in **1** act not as bridging ligands, but rather as extraframework guest molecules. The Cu^+ center, which is formed through the reduction of Cu^{2+} under hydrothermal conditions,[8] has tetrahedral coordination geometry and is surrounded by four N donors of four 4,4′-bipyridine (4,4′-bipy) ligands. The 4,4′-bipy ligands bridge tetrahedral Cu^+ centers to form a twofold interpenetrating diamond framework. The positively charged framework of **1** is charge-balanced by guest D-Hcam anions. Despite the twofold

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Table 1: Crystal data and refinement results.

	Formula	Space group	*a* [Å]	*b* [Å]	*c* [Å]	*β* [°]	*R*(*F*)	Flack parameter
1	$[Cu_2(4,4\text{-bipy})_4]\cdot(\text{D-Hcam})_2\cdot(4,4'\text{-bipy})_2\cdot 12\,H_2O$	$P2_1$	11.556(1)	25.628(1)	14.100(1)	94.144(2)	0.0556	0.03(2)
2	$[Cd_4(OH)(\text{D-cam})_4(H_2O)_2]\cdot\text{Hdma}\cdot\text{dma}$	*I*222	13.447(1)	13.944(1)	14.280(1)	90	0.0674	0.13(17)
3[a]	$[Cd_4(OH)(\text{D-cam})_4(\text{py})]\cdot\text{Hdma}$	*C*2	19.525(2)	13.916(2)	13.302(1)	132.94(2)	0.0639	−0.31(11)
		*I*2	13.317(2)	13.923(1)	14.303(1)	90.484(4)		
4[a]	$[Co_4(OH)(\text{D-cam})_4(\text{py})]\cdot\text{Hdma}$	*C*2	18.799(3)	13.813(2)	13.153(2)	134.40(2)	0.0554	0.09(3)
		*I*2	13.1605(5)	13.8194(6)	13.4271(9)	90.875(2)		
5	$[Cd_2(\text{D-cam})_3]\cdot 2\,\text{Hdma}\cdot 4\,\text{dma}\cdot 2\,H_2O$	$P4_22_12$	13.400(1)	13.400(1)	24.367(1)	90	0.0600	−0.09(10)

[a] Structures of **3** and **4** are refined in the standard space group *C*2. The unit cells for the nonstandard *I*2 setting are given to show the isostructural relationship with compound **2**.

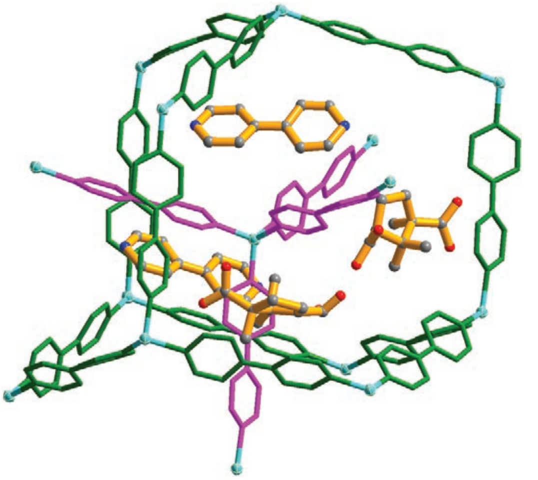

Figure 1. View of the organic guest molecules (two D-Hcam and two 4,4′-bipy species, each shown with yellow bonds; for these species: N blue, O red, C gray) in a twofold interpenetrating diamond net of **1**; Cu is shown in blue.

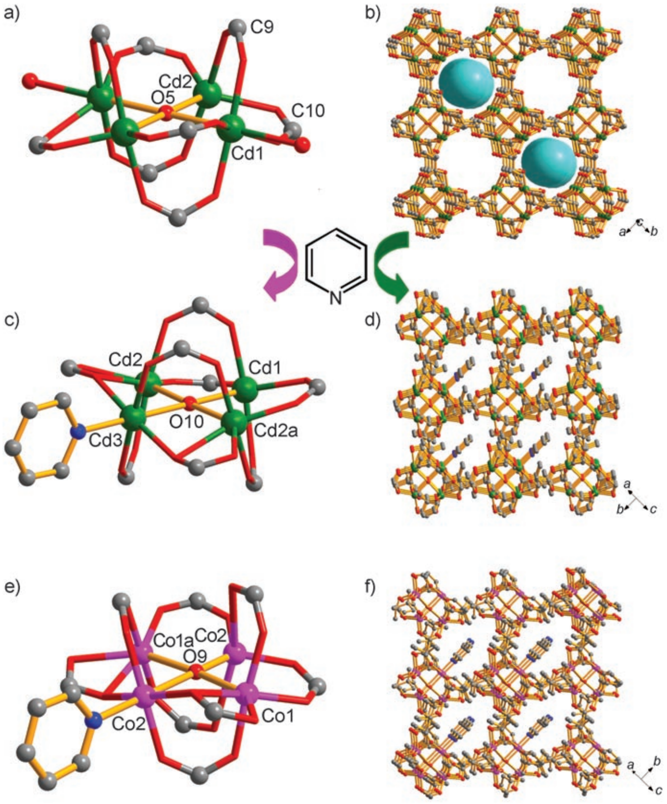

Figure 2. a) Simplified view of the $\{Cd_4(OH)\}$ square in **2**. b) The homochiral microporous framework in **2**, showing the cylindrical channels along the *c* axis. Two sky-blue spheres are used to illustrate the void regions in the channels. c) Simplified view of the $\{Cd_4(OH)\}$ square in **3**. d) The homochiral framework of **3**. e) Simplified view of the $\{Co_4(OH)\}$ square in **4**. f) The homochiral framework of **4**.

interpenetration, **1** still possesses 3D open channels that can accommodate a significant amount of guest species: two 4,4′-bipy molecules, two D-Hcam anions, and 12 water molecules per asymmetric unit.

A prominent structural feature in **2**–**4** is the presence of a novel inorganic $\{M_4(OH)\}$ (M = Cd or Co) square (Figure 2a,c,e). A bond-valence calculation[9] indicates that the bond-valence sums from the center O atom to its adjacent M^{2+} sites are 1.17 in **2**, 1.16 in **3**, and 1.23 in **4**, which suggests that the center O atom in each solid is "underbonded" in the absence of a proton and that it should be a hydroxy group.

Compound **2** crystallizes in the chiral space group *I*222. As shown in Figure 2a, there are two Cd sites per asymmetric unit and both reside on the twofold axis. At the center of the Cd_4 square is a hydroxy species located at the intersection of three mutually perpendicular twofold axes. Cd1 adopts a distorted octahedral geometry and is coordinated by four O atoms of four D-cam ligands, one μ_4-OH ligand, and one weakly coordinated aqua ligand (Cd−O 2.58(3) Å). Cd2 adopts a distorted trigonal-bipyramidal geometry and is coordinated by four O atoms of four D-cam ligands and one μ_4-OH ligand. The shortest Cd···Cd separation is 3.3362(8) Å. The unusual $\{Cd_4(OH)\}$ square is stabilized by eight bidentate bridging chiral carboxylate groups from eight directions, and together they serve as an eight-connected node in the structure.

Compound **2** exhibits the 3D homochiral open framework with a body-centered cubic topology. Figure 2b shows the cylindrical channels with diameter of 9.21 Å. These channels propagate along the *c* axis and are filled with disordered Hdma cations and dma molecules (dma = dimethylamine). The solvent-accessible volume is approximately 555.2 Å^3 per unit cell, and the pore volume ratio was calculated to be 20.7% using the PLATON program.[10]

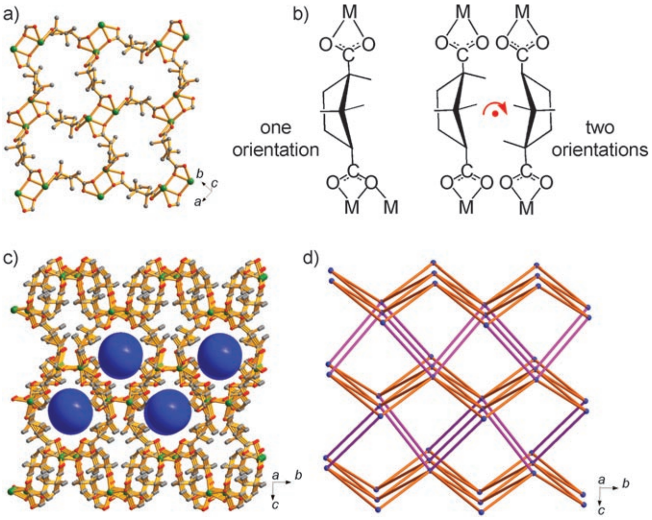

Figure 3. a) The (4,4) layer in **5**. b) Schematic representation of the coordination modes of the ordered D-cam ligand and disordered D-cam ligand related through a twofold axis. c) The homochiral open framework in **5**, showing the cylindrical channels along the *a* axis. Four blue spheres are used to illustrate the open regions in the channels. d) Schematic representation of the six-connected $4^7.6^8$ net in **5**. The purple lines represent the disordered D-cam ligands while orange lines represent ordered D-cam ligands.

Compound **2** can undergo solvent-exchange-induced single-crystal to single-crystal transformation. Upon immersion of **2** in a solvent mixture of DMF/C_2H_5OH/pyridine at 100 °C for 8 h, the coordinated water molecule in **2** is exchanged by the solvent pyridine (py) molecule to give compound **3**, as confirmed by single-crystal X-ray diffraction.

In addition to the synthesis by solvent exchange, compound **3** can also be crystallized upon direct solvothermal synthesis. Compound **3** is also constructed from eight-connected square {$Cd_4(OH)$} units (Figure 2c) and is topologically equivalent to **2**. It is worth noting that in compound **2**, there are two aqua ligands bonded to each {$Cd_4(OH)$} unit, whereas in **3**, there is only one pyridine ligand attached to the {$Cd_4(OH)$} unit. Furthermore, compound **2** has twice as many extraframework dma molecules (charged plus neutral) as that in compound **3** (charged only). This result is apparently because the aqua or pyridine ligands protrude into the channel, and the size of the channel becomes smaller with the larger pyridine ligand (Figure 2d). The exchange of two aqua ligands by one pyridine ligand also helps to lower the symmetry from *I*222 for the aqua form **2** to *C*2 (or *I*2) for the pyridine form **3**.

In **3**, the twofold axis runs through the Cd1-O10-Cd3 linkage and bisects the pyridine ligand (Figure 2c). Three crystallographically unique Cd sites with trigonal-bipyramidal (Cd1) and distorted octahedral (Cd2 and Cd3) geometries are present. Only the Cd3 site is coordinated by the pyridine N atom. The adjacent Cd⋯Cd separations are 3.269 (Cd1⋯Cd2) and 3.381 Å (Cd2⋯Cd3). The {$Cd_4(OH)$} square is also stabilized by eight carboxylate groups from eight directions. The anionic framework of **3** is charge-balanced by guest Hdma cations residing in chiral channels that propagate along the [111] direction (Figure 2d).

Compound **4** is isostructural to **3.** The replacement of Cd^{2+} in **3** by Co^{2+} in **4** results in a slightly smaller unit cell. The observation of a square-planar {$M_4(OH)$} unit for both Co and Cd is unusual because the {$M_4(OH)$} unit known in the literature is generally nonplanar.

Compound **5** crystallizes in the chiral space group $P4_22_12$ and exhibits an unprecedented six-connected net. In **5**, the Cd center is seven-coordinated by four carboxylate groups from four different D-cam ligands. The Cd–O bond lengths range from 2.274(11) to 2.508(13) Å. There are two independent D-cam ligands with different coordination modes. One D-cam ligand is ordered while the second one has two statistical orientations related through a twofold axis (Figure 3b). The ordered D-cam ligands connect the dinuclear Cd units into wavelike (4,4) sheets (Figure 3a), which are further pillared up by the disordered D-cam ligands. The resulting 3D framework contains large 2D intersecting channels along the *a* and *b* axes (Figure 3c). The solvent-accessible volume is approximately 1462.3 Å^3 per unit cell, and the pore volume ratio was calculated to be 33.4% using the PLATON program.[10]

In **5**, the dinuclear Cd unit is surrounded by four ordered D-cam ligands and two disordered D-cam ligands and therefore serves as a six-connected node in the structure. The whole framework can be topologically represented as a six-connected net with a vertex symbol of $4.4.4.4.4.4.4.4.6_4.6_8.6_4.6_4.6_4.6_5.6_7.6_4$ and a short Schläfli symbol of $4^7.6^8$.[11] As shown in Figure 3d, this net consists of wavelike (4,4) sheets (orange) cross-linked by zigzag chains (purple). It is different from other reported six-connected nets that tend to contain rather planar (4,4) sheets.[12] Another interesting aspect of this six-connected net is that it is similar to the bcu net and can be derived from the bcu net (Figure S4 in the Supporting Information) by breaking two connectors from each node in the eight-connected net. The free space in this six-connected net is therefore larger than that in the eight-connected bcu net.

The thermal analysis on compounds **2**–**4** shows two distinct stages of weight loss for all of them (details in the Supporting Information). The first stage corresponds to the loss of extraframework guest molecules or weakly coordinated ligands (water or pyridine). While these compounds exhibit open channels, the nitrogen sorption studies at liquid-nitrogen temperature on compounds **2** and **5** do not show microporous behavior (type I isotherm). The X-ray powder diffraction studies on samples before and after the sorption studies show that upon the loss of extraframework or weakly coordinating ligands, phase transitions into new and yet still unidentified crystalline phases have occurred (Figure S10, S13 in the Supporting Information), which likely reduce the pore size and accessible surface areas. Furthermore, it is also known that some metal–organic frameworks that exhibit permanent microporosity were found to be nonporous to nitrogen at 77 K.[3b]

In summary, we demonstrate that the versatile zeolite synthetic approach (templating by charged organic structure directing agents) can be extended to the direct self-assembly of enantiopure molecular precursors into 3D homochiral metal–oragnic frameworks, as shown by four organic cation templated homochiral frameworks with six- and eight-connected open-framework topologies. In addition, we present here an unusual enantiopure organic anion (chiral carboxylate) templated four-connected framework in **1**. Three of the materials (compounds **2**–**4**) contain an unusual $\{M_4(OH)\}$ ($M = Cd^{2+}$ and Co^{2+}) square-planar building block.

Experimental Section

1: $Cu(NO_3)_2{\cdot}3H_2O$ (0.1559 g), 4,4′-bipyridine (0.1665 g), D-(+)-camphoric acid (0.0995 g), and distilled water (8.1038 g) were mixed in a 23-mL teflon cup, and the mixture was stirred for 20 min. The vessel was then sealed and heated at 190 °C for 3 days. The autoclave was subsequently allowed to cool to room temperature. After washing with ethanol and distilled water, red crystals were obtained.

2: D-Camphoric acid (0.0500 g, 0.25 mmol), dimethylamine (40 % w/w aqueous solution, 0.1034 g), and $Cd(NO_3)_2{\cdot}4H_2O$ (0.0792 g, 0.25 mmol) in a solvent mixture of DMF (1.8129 g) and C_2H_5OH (0.7824 g) were placed in a vial. The sample was heated at 100 °C for 24 h and then cooled to room temperature. After washing with ethanol and distilled water, colorless crystals were obtained in 76 % yield. Elemental analysis (%) calcd for **2** ($C_{44}H_{80}Cd_4N_2O_{19}$): C 38.00, N 2.01, H 5.80; found: C 38.02, N 2.10, H 5.50.

3: D-Camphoric acid (0.0517 g), dimethylamine (40 % w/w aqueous solution, 0.0945 g), and $Cd(NO_3)_2{\cdot}4H_2O$ (0.0859 g) in a solvent mixture of DMF (1.9428 g), C_2H_5OH (1.4963 g), and pyridine (0.0701 g) were placed in a vial. The sample was heated at 100 °C for 2 days and then cooled to room temperature. After washing with ethanol and distilled water, colorless crystals were obtained in 89 % yield. Elemental analysis (%) calcd for **3** ($C_{47}H_{69}Cd_4N_2O_{17}$): C 40.80, N 2.02, H 5.03; found: C 40.83, N 2.08, H 5.21.

4: D-Camphoric acid (0.1081 g) and $Co(NO_3)_2{\cdot}6H_2O$ (0.1623 g) in a solvent mixture of DMF (1.5223 g), butanol (1.5921 g), and pyridine (0.0672 g) were placed in in a 23-mL teflon cup. The vessel was then sealed and heated at 160 °C for 7 days. The autoclave was subsequently allowed to cool to room temperature. After washing with ethanol and distilled water, purple crystals were obtained in 89 % yield.

5: D-Camphoric acid (0.1050 g), (*S*)-(+)-2-methylpiperazine (0.0263 g), and $Cd(NO_3)_2{\cdot}4H_2O$ (0.1501 g) in a solvent mixture of DMF (1.8366 g) and C_2H_5OH (0.9524 g) were placed in a 23-mL teflon cup. The vessel was then sealed and heated at 100 °C for 10 days. The autoclave was subsequently allowed to cool to room temperature. After washing with ethanol and distilled water, colorless crystals were obtained in 86 % yield. Elemental analysis (%) calcd for **5** ($C_{42}H_{100}Cd_2N_6O_{14}$): C 44.32, N 7.38, H 8.86; found: C 44.40, N 7.60, H 8.02.

Thermal analysis: The simultaneous DSC–TGA thermal analysis was performed on TA Instruments SDI Q600 under a flow of nitrogen. The flow rate of the nitrogen gas was controlled at about 100 mL min^{-1}. A total of 13.9230 mg of **2**, a total of 11.6680 mg of **3**, a total of 4.8300 mg of **4**, and a total of 8.3290 mg of **5** were heated in four separate runs between room temperature and 800 °C (700 °C) at a heating rate of 10 °C min^{-1}.

X-ray powder diffraction: X-ray powder diffraction experiments were performed on a Bruker D8 Advance X-ray powder diffractometer operating at 40 kV and 40 mA ($Cu_{K\alpha}$ radiation, $\lambda = 1.5418$ Å). The data collection was carried out with a step size of 0.03° and counting time of 1 s per step. The 2θ angular range is 5–35°.

Nitrogen adsorption: N_2 sorption analysis was performed on a Micromeritics ASAP2010 volumetric adsorption analyzer at 77 K.

CCDC-652574–652577 (**2**–**5**) and 652578 (**1**) 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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