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Self-Assembly of Homochiral Porous Solids Based on 1D Cadmium(II) Coordination Polymers

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A family of homochiral 1D cadmium(II) coordination polymers based on the (*S*)-2,2′-dimethoxy-1,1′-binaphthyl-3,3′-bis(4-vinylpyridine) (**L**) bridging ligand were synthesized from the same building blocks under slightly different conditions, and characterized by single-crystal X-ray crystallography. While $[\mathrm{Cd}\mathbf{L}(\mathrm{DMF})_4](\mathrm{ClO}_4)_2\cdot\mathrm{EtOH}\cdot0.5\mathrm{H}_2\mathrm{O}$ (**1**) adopts a 1D zigzag chain structure, $[\mathrm{Cd}\mathbf{L}_2(\mathrm{ClO}_4)_2]\cdot3\mathrm{EtOH}\cdot\mathrm{H}_2\mathrm{O}$ (**2**) and $[\mathrm{Cd}\mathbf{L}_2(\mathrm{ClO}_4)(\mathrm{H}_2\mathrm{O})]\ (\mathrm{ClO}_4)\cdot1.5(o\text{-}\mathrm{C}_6\mathrm{H}_4\mathrm{Cl}_2)\cdot3\mathrm{EtOH}\cdot6\mathrm{H}_2\mathrm{O}$ (**3**) both exhibit 1D polymeric structures that are built from 38-membered macrocycles. These 1D coordination polymers further pack into chiral porous frameworks via $\pi\cdots\pi$ interactions with a large percentage of void spaces that are occupied by solvent molecules and counterions.

The design and synthesis of homochiral coordination networks with accessible chiral pores or functionalities has been actively pursued over the past few years.[1] Such homochiral porous solids are potentially useful for enantioselective separations and catalysis.[2] We have recently successfully demonstrated the applications of amorphous metal-phosphonates in heterogeneous asymmetric hydrogenation with practically useful catalytic activity and enantioselectivity.[3] In order to have a better understanding of the structural features of homochiral coordination networks, we have examined the self-assembly of homochiral coordination networks based on the (*S*)-2,2′-dimethoxy-1,1′-binaphthyl-3,3′-bis(4-vinylpyridine) (**L**) bridging ligand and different metal nodes.[4] Herein we wish to report the synthesis and characterization of three new homochiral 1D polymers, $[\mathrm{Cd}\mathbf{L}(\mathrm{DMF})_4](\mathrm{ClO}_4)_2\cdot\mathrm{EtOH}\cdot0.5\mathrm{H}_2\mathrm{O}$ (**1**), $[\mathrm{Cd}\mathbf{L}_2(\mathrm{ClO}_4)_2]\cdot3\mathrm{EtOH}\cdot\mathrm{H}_2\mathrm{O}$ (**2**), and $[\mathrm{Cd}\mathbf{L}_2(\mathrm{ClO}_4)(\mathrm{H}_2\mathrm{O})]\text{-}(\mathrm{ClO}_4)\cdot1.5(o\text{-}\mathrm{C}_6\mathrm{H}_4\mathrm{Cl}_2)\cdot3\mathrm{EtOH}\cdot6\mathrm{H}_2\mathrm{O}$ (**3**). These structurally distinct coordination networks based on the same building blocks were obtained under slightly different reaction (crystal growth) conditions.

Enantiopure **L** was synthesized according to our previously published procedures.[4a] Single crystals of **1** were obtained by slowly diffusing diethyl ether into a mixture of $\mathrm{Cd}(\mathrm{ClO}_4)_2\cdot6\mathrm{H}_2\mathrm{O}$ and **L** in DMF/o-$\mathrm{C}_6\mathrm{H}_4\mathrm{Cl}_2$/EtOH.[5] An X-ray analysis[6] showed that compound **1** is a 1D zigzag coordination polymer formed by linking DMF-coordinated Cd(II) centers with **L** bridging ligands (Figure 1).[6] Each Cd(II) center is octahedrally coordinated to two nitrogen atoms of two different **L** ligands and four oxygen atoms of four DMF molecules. The two nitrogen atoms of the two **L** ligands on each Cd(II) center are *cis* to each other ($\mathrm{Cd-N} = 2.277(8)$ and $2.318(10)$ Å, and $\mathrm{N-Cd-N} = 95.3(3)°$). Such a *cis*

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(5) Synthesis of $[\mathrm{CdL}(\mathrm{DMF})_4][\mathrm{ClO}_4]_2\cdot\mathrm{EtOH}\cdot0.5\mathrm{H}_2\mathrm{O}$ (**1**). Slow diffusion of diethyl ether into a mixture of $\mathrm{Cd}(\mathrm{ClO}_4)_2\cdot6\mathrm{H}_2\mathrm{O}$ (4.2 mg, 0.01 mmol), **L** (5.2 mg, 0.01 mmol), DMF (2 mL), $\mathrm{C}_6\mathrm{H}_4\mathrm{Cl}_2$ (1 mL), and EtOH (1 mL) for 1 week led to colorless crystals of **1**. The colorless crystals of **1** were filtered, washed with EtOH and $\mathrm{Et}_2\mathrm{O}$, and dried at room temperature. Yield: 3.9 mg (33.1%). No reliable microanalysis results can be obtained for **1** owing to the ready loss of included solvent molecules during the sample transport process. IR (KBr pellet, cm^{-1}): 3439br, 3061w, 2931w, 1657s, 1608s, 1500w, 1435sh, 1384s, 1297w, 1237m, 1099s, 1007m, 980w, 876w, 761m, 727w, 661w, 623w. Synthesis of $[\mathrm{CdL}_2(\mathrm{ClO}_4)_2]\cdot2\mathrm{EtOH}\cdot\mathrm{H}_2\mathrm{O}$ (**2**). A mixture of $\mathrm{Cd}(\mathrm{ClO}_4)_2\cdot6\mathrm{H}_2\mathrm{O}$ (4.2 mg, 0.01 mmol), **L** (5.2 mg, 0.01 mmol), DMF (2 mL), $\mathrm{C}_6\mathrm{H}_4\mathrm{Cl}_2$ (1 mL), and EtOH (1 mL) in a capped vial was heated at 70 °C for 4 days. Colorless crystals of **2** were filtered, washed with EtOH and $\mathrm{Et}_2\mathrm{O}$, and dried at room temperature. Yield: 4.3 mg (57.0% based on **L**). Anal. Calcd for **1** (%): C, 62.1; H, 5.08; N, 3.71. Found: C, 59.6, H, 4.83, N, 3.34. IR (KBr pellet, cm^{-1}): 3448br, 3056w, 1607s, 1549w, 1500m, 1456m, 1429m, 1357m, 1236m, 1103s, 1033m, 1015m, 974w, 922w, 859w, 753m, 622m. Synthesis of $[\mathrm{CdL}_2(\mathrm{ClO}_4)(\mathrm{H}_2\mathrm{O})][\mathrm{ClO}_4]\cdot1.5(\mathrm{C}_6\mathrm{H}_4\mathrm{Cl}_2)\cdot3\mathrm{EtOH}\cdot6\mathrm{H}_2\mathrm{O}$ (**3**). Compound **3** was synthesized similarly to **2** except two additional drops of water (~0.1 mL) were added to the reaction mixture. Yield: 4.9 mg (53.3% based on **L**). Anal. Calcd for **3** (%): C, 56.9; H, 5.16; N, 3.05. Found: C, 54.9, H, 4.56, N, 3.59. IR (KBr pellet, cm^{-1}): 3462br, 3055w, 1607s, 1550w, 1500m, 1456m, 1429m, 1384w, 1357m, 1236m, 1107s, 1034w, 1014m, 975w, 924w, 859w, 813w, 787w, 754m, 623m.

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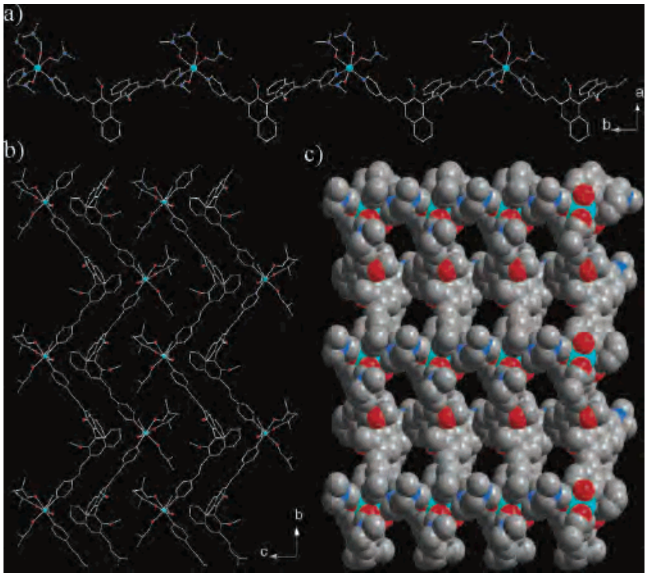

Figure 1. (a) The 1D zigzag chain of **1**. (b) A view of the packing of 1D zigzag chains of **1** down the *c* axis. (c) Space-filling model of **1** showing large open channels along the 101 direction. Cd, N, O, and C atoms are shown in cyan, blue, red, and gray, respectively.

linking mode is different from the *trans* linking mode that was observed in a triple helical Ni(acac)$_2$(**L**) coordination polymer.[4a] The binaphthyl rings of **L** are twisted along the pivotal 1,1′-bond with a dihedral angle of 86.3°. It is very interesting that the neighboring chains are linked to each other via $\pi\cdots\pi$ interactions (the nearest carbon to carbon separation of 3.47 Å) to lead to a 3D supramolecular framework. The network yields 1D chiral channels with dimensions about 8.0 × 9.2 Å^2 along the 101 direction. Calculations using PLATON[7] revealed that the open channels constitute about 31.8% (960.3 Å^3 out of 3019 Å^3) of the crystal volume and are filled with ClO_4^- anions and EtOH and H_2O solvent molecules.

When a mixture of $Cd(ClO_4)_2\cdot 6H_2O$ and **L** in DMF/*o*-$C_6H_4Cl_2$/EtOH in a capped vial was heated at 70 °C, large plate-shaped colorless crystals of **2** were obtained. A single X-ray diffraction study revealed that **2** adopts a 1D polymeric structure that results from linking of 38-membered macrocycles by Cd(II) ions (Figure 2). Each Cd(II) center sits on a 2-fold axis and coordinates to four N atoms of four **L** ligands in the equatorial plane (Cd−N = 2.36(2)−2.39(2) Å), and two O atoms of two perchlorate anions lying on the axial positions (Cd−O = 2.12(3) Å). The dihedral angle between the naphthyl subunits in **2** is 85.8°, which is similar to that of **1**. In stark contrast to the structural motif of **1**, two **L** ligands in **2** link two Cd(II) centers to form a 38-membered macrocycle with a Cd(II)−Cd(II) distance of 19.31 Å. These macrocycles are then propagated by the Cd(II) nodes into 1D chains, which further packed into **2** via $\pi\cdots\pi$ interactions with the nearest carbon to carbon separation of 3.705 Å. Large chiral open channels of dimensions of 9.9 × 12.2 Å^2 were generated along the 110 direction (Figure 2). These open channels constitute ~45.2% (2244.9 Å^3) of the crystal volume (PLATON) and are occupied by the EtOH and H_2O solvent molecules.

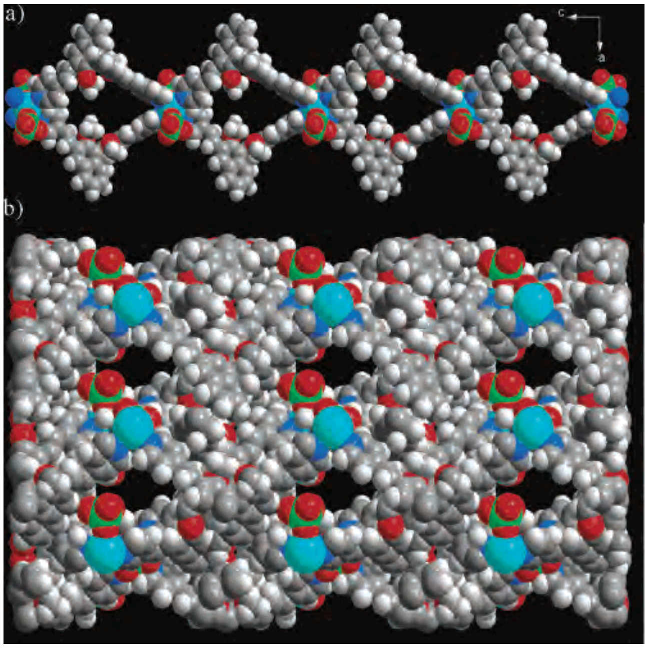

Figure 2. (a) Space-filling representation of the 1D polymeric chain built up from 38-membered macrocycles in **2**. (b) Space-filling model of **2** showing large open channels along the 110 direction. Cd, N, O, C, and H atoms are shown in cyan, blue, red, medium gray, and light gray, respectively.

Interestingly, small colorless parallelepiped crystals of **3** were obtained when a small amount of water was added into the reaction mixture of **2**. A single-crystal diffraction study has established that crystals of **3** have a different composition from **2**. Just like **2**, **3** also adopts a 1D coordination polymeric structure that is built up from 38-membered macrocycles. The Cd(II) centers in **3**, however, coordinate to an aqua ligand instead of a perchlorate anion in one of the axial positions. The Cd(II) center thus adopts a slightly distorted octahedral coordination environment by coordinating to four N atoms of four **L** ligands (Cd−N = 2.30 (2)-2.34(1) Å), one O atom of a perchlorate anion (Cd−O = 2.47(2) Å), and an aqua ligand (Cd−O = 2.40(1) Å). The change of the coordination environment of Cd(II) centers has significant structural consequences in the 3D architecture of **3** (Figure 3). Compound **3** crystallizes in a different space group ($C222_1$) from **2** ($P2_12_12$). The dihedral angles of two independent binaphthyl subunits in **3** are 79.4° and 83.8°, which are slightly smaller than that of **2**. Strong $\pi\cdots\pi$ interactions (the nearest C···C distance of 3.579 Å) and $\pi\cdots$edge interactions (the nearest C···C distance of 3.525 Å) link the 1D macrocycles in **3** into a 3D open framework with large channels along the *a* axis (8.0 × 16.0 Å^2) and the 110 direction (6.6 × 16.7 Å^2) (Figure 3). PLATON calculations

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(6) Crystallographic data for **1**: monoclinic, space group $P2_1$, $a = 10.377(5)$ Å, $b = 18.774(9)$ Å, $c = 16.048(7)$ Å, $\beta = 105.06(6)°$, $U = 3019(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.297$ g cm^{-3}, μ(Mo Kα) = 0.515 mm^{-1}, $R1 = 0.0908$, $wR2 = 0.232$, Flack parameter = 0.04(5) and GOF = 1.06. For **2**: orthorhombic, space group $P2_12_12$, $a = 14.430(1)$ Å, $b = 17.817(1)$ Å, $c = 19.307(1)$ Å, $U = 4963.9(5)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.009$ g cm^{-3}, μ(Mo Kα) = 0.326 mm^{-1}, $R1 = 0.123$,, $wR2 = 0.296$, Flack parameter = 0.03(1) and GOF = 1.02. For **3**: orthorhombic, space group $C222_1$, $a = 17.672(1)$ Å, $b = 34.118(1)$ Å, $c = 32.348(1)$ Å, $U = 19503.3(8)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.251$ g cm^{-3}, μ(Mo Kα) = 0.428 mm^{-1}, $R1 = 0.119$, $wR2 = 0.264$, Flack parameter = 0.1(1) and GOF = 1.20.

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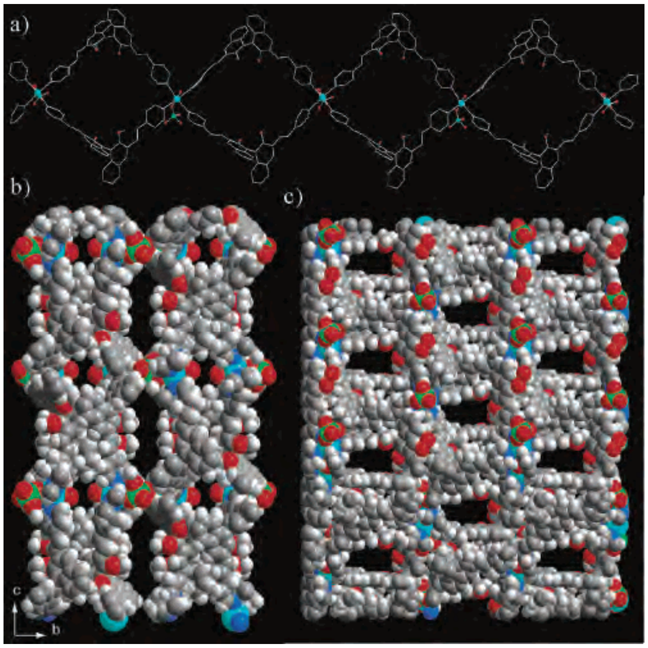

Figure 3. (a) A vew of the 1D polymeric chain in **3**. (b) Space-filling model of **3** showing large channels along the *a* axis. (c) Space-filling model of **3** showing large channels along the 110 direction. Cd, N, O, C, and H atoms are shown in cyan, blue, red, medium gray, and light gray, respectively.

indicated that 47.9% of the crystal volume (9334.9 Å^3 out of 19503 Å^3) is occupied by perchlorate anion and dichlorobenzene, ethanol, and water molecules.

Thermogravimetric analyses (TGA) showed that **1** lost 4.65% of total weight in the 20−65 °C temperature range, corresponding to the loss of half water and one EtOH molecules per formula unit (expected 4.67%), and further lost 25.5% of total weight by 330 °C, corresponding to the loss of four coordinating DMF molecules (expected 24.8%). TGA indicated that **2** experienced 10.5% weight loss in the 20−240 °C temperature range for one water and three EtOH molecules per formula unit (expected 10.4%), while **3** exhibited weight loss of 25.3% in the 20−340 °C temperature range for 1.5 $C_6H_4Cl_2$, 3 EtOH, and 6 H_2O molecules per formula unit (expected 25.4%). X-ray powder diffraction studies indicated bulk sample of **1** was essentially amorphous, presumably due to the ready loss of the solvents (Supporting Information). In contrast, sharp powder diffraction patterns were obtained for both **2** and **3**. Compounds **2** and **3** lose their long-range order upon the removal of included solvent molecules by heating under vacuum, but their crystallinity can be restored by immersing the evacuated samples in EtOH.

In conclusion, we have obtained three structurally distinct homochiral 1D coordination polymers from the same building blocks under slightly different reaction (crystal growth) conditions. Such structural diversities provide an additional tunable parameter for the synthesis of homochiral porous solids for potential applications in chiral separations and asymmetric catalysis.

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Supporting Information Available: One table and 18 figures, and X-ray crystallographic files (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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